


# PHOTOGRAPHY WITH EMULSIONS:

A TREATISE ON  
THE THEORY AND PRACTICAL WORKING OF  
Gelatine and Colloidion Emulsion Processes,  
By Captain W. DE W. ABNEY, R. E., F. R. S.

SCOVILL MANUFACTURING COMPANY,  
NEW YORK.

W. IRVING ADAMS, Agent.











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# PHOTOGRAPHY WITH EMULSIONS.

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## CHAPTER I.

### PRELIMINARY CONSIDERATIONS.

THE term emulsion is derived from the Latin word "emulgere," to milk out, and the definition of it as found in the dictionary is, "any milk-like mixture prepared by uniting oil and water by means of another substance." For our photographic technology this is hardly a correct definition, for by it we mean a sensitive salt of silver in very minute division, held in suspension in some viscous body, such as gelatine, or, more commonly, collodion.

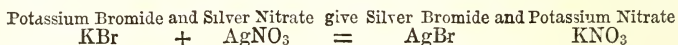
An emulsion in its simplest form may be considered to be simply a pure silver haloid held in suspension in collodion or gelatine, and so well prepared that when a plate is coated with it, a homogeneous film results; a film which, in fact, is at least equal in sensitiveness and in physical qualities to any which can be prepared by any other process.

Emulsion processes are divided into two classes: one in which the emulsion is made up and used without any preliminary extraction of the soluble salts which are necessarily present in their manufacture, owing to the

double decomposition of the salts employed, &c., and the silver nitrate; and the other where these soluble salts are extracted. In the first process the plates are washed after coating, and is usually confined to collodion emulsions; whilst in the second they are coated, and generally left to dry spontaneously.

We may say that all emulsions at present in vogue may be considered to be simply bromide of silver, since it is the basis on which all alterations by the addition of iodide or chloride are to be made. It will be seen in the context that these additions are not unimportant as regards the range of sensitiveness.

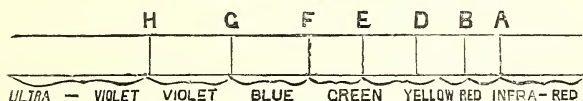
The universal mode of production in emulsion is to dissolve certain soluble bromides (such as potassium bromide) in the collodion or in a gelatine solution, and then to gradually pour a solution of silver nitrate dissolved in alcohol and water in the first case, or in water alone in the second, into the viscous fluid, by which means solid bromide of silver is formed, together with a soluble nitrate (such as potassium nitrate). It is this latter soluble product which in washed emulsions is removed, since, if a film be left to dry without eliminating it, crystallization sets up, and the surface of the coated plate is spoilt. Silver chloride is readily emulsified in the same way, substituting a soluble chloride (such as of sodium) for the soluble bromide. Silver iodide is also easily formed into an emulsion in gelatine, but it is formed with much more difficulty in collodion. We give the chemical equation for the formation of silver bromide.



Bromide of silver may be produced in several molecular states, all of which have different degrees of sensitiveness. When we say different molecular states, we mean that the silver bromide has precisely the same chemical composition, but that it is altered physically, the molecules

being larger in some cases than others; the tangible molecule being built up of a greater or less number of primary molecules, according to the rapidity of the formation of the solid, and its subsequent treatment by heat, ammonia, &c. Thus, it is known that transmitted light, as seen through a film, may appear of a ruby, orange, green, purple, or grey colour; and of these, three seem to be different states of molecular aggregation—viz., ruby, green, and grey; the others are probably mixtures of one or more of the three. We must assume that the reader is aware what a spectrum is. By exposing any of these modifications to its action we find that the range of sensitiveness to the different coloured rays is varied. Thus the

## PRISMATIC SPECTRUM.

*Fig. 1.*

ruby and orange modification is sensitive to the ultra violet, the violet, and blue rays, and a little in the green; the grey blue is sensitive to the same rays, but more strongly in the green, whilst it is able to be impressed by the yellow and by the red rays; the green modification, when in collodion, is sensitive to the ultra violet; the blue, very slightly to the green, and much more so to the red, and infra red region, *i.e.*, those dark rays which are mis-called the heat rays.

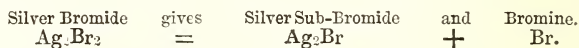
In collodion emulsion the ruby and orange form of bromide is that most sought after, whilst in gelatine emulsion the form which is supposed to give the most sensitive films is the blue grey form; though for our own part we consider that a tinge of yellow is essential to get the highest sensitiveness. The reason for selecting these forms we shall touch upon by-and-bye.

Iodide of silver in its pure state is sensitive only to the ultra violet, the violet, and the blue rays, and just to the margin of in green, and it may well be supposed that by adding iodide to the bromide some modification of the range of spectral sensitiveness must be found. Such is the case, and it is more marked in gelatine emulsion, in which, were no iodide added, the emulsion would take the blue grey state.

If we add 4 per cent of iodide of silver to the bromide in a gelatine plate, the sensitiveness is diminished in the red rays, and the yellow rays will not impress themselves, except by very prolonged exposure. If we add 8 per cent., the green rays are with the greatest difficulty impressed, where with 12 per cent. the rays which can impress themselves are confined to the part of the spectrum to which the iodide *per se* is sensitive.

Chloride of silver modifies the photographic qualities of the bromide but little, and since it is but rarely used in any quantity, we need not consider it.

*Chemical Composition of the Developable Image.*—Evidence of the most unmistakable character points to the chemical theory of the formation of the photographic image—evidence so strong, and so well known, that it would be out of place to record it here. Briefly we may say that the action of light on a silver haloid seems to be to reduce it to a simpler type, which we may call the sub-haloid. Thus



If any reader will not admit it, he should read all the various evidence that has been adduced since the time when Scheele first made his experiments with silver chloride, and we doubt if he can remain unconvinced, more particularly in regard to the visible image formed on the bromide and chloride. It is a pertinent question to put, as to whether the visible and the invisible (or developable) image are of the same nature; which may be answered

by another question : Can the line be drawn where the image is invisible ? If so, what is the boundary between the two ? If we admit the theory of the formation of the visible image, it seems hardly logical to deny a similar formation for the invisible or photographic image. It is quite possible that beings with more acute sight than ourselves might be able to see the image which we cannot, as we know certain insects can hear sounds which do not affect our auditory nerves. Coloured particles are visible, when put together *en masse*, but if only a few coloured particles are present in a mass of colourless particles, it is quite certain that they may remain undetected.

If we may, then, be allowed to beg the question, or rather to assume that silver bromide is reduced by light to the sub-bromide as indicated, the following paragraph will be understood.

*The Cause and Cure of Fog in Emulsions.*—Every student in emulsion work has found, and will find, that the chief obstacle that he has to overcome is the tendency for the plates prepared with it to fog on development, and it has taken a great deal of experimental work to enable it to be overcome. The reason of the fog-giving emulsion has been obscure ; but the writer ventures to think that the recent researches that have been made on the subject have explained in a great measure, if not entirely, its *raison d'être*, and, in spite of being tedious, or of being told that the reader knows all about it, a summary of what is known of the matter is appended.

Setting aside the collodion or gelatine from the question, and merely taking into consideration the sensitive salts employed, we may arrive at very definite results. It has been asserted that a neutral combination between two substances can never take place ; for example, if we mix potassium chloride with silver nitrate we shall never be able to get pure silver chloride, however much we may wash it—that either the soluble potassium or silver salt will always be in excess, though in the minutest quan-

tities. This certainly is the case theoretically, because do what you will, and wash as long as you like, there still must be some infinitely small part of the soluble salt left behind. Now, for ordinary chemical reactions, where the products of these combinations have to be weighed, the residual impurity may be inappreciable, being so infinitesimal that no balance yet constructed can show them. Though a balance may be inoperative, yet, as is well known, light is able to show us impurities in a substance which may not be one-millionth part of a grain in weight. By passing the light from the heated vapours of the substance and its impurity through a prism, and noting its spectrum, we may be able to detect the latter.

The spectroscopie will not tell us at present, however, whether the silver or potassium is present as nitrate, chloride, bromide, oxide, &c.

The question now arises, is it possible to detect this? Is it possible, for instance, to say whether any infinitesimal quantity of oxide be present? In the majority of cases the question would be an open one; but where we are dealing with silver salts which are sensitive to light, and which are amenable to development, we think we can give an affirmative answer. Sometimes, however, the impurities in the bromides can be shown by weighing. For, in a paper read before the Photographic Society of Great Britain on the 8th of February, 1876, Mr. Warnerke stated that on testing the different bromides, he found that considerable variation from the theoretical quantities necessary to combine with silver nitrate was observable. Thus he found that one grain of silver nitrate requires

Of potassium bromide	1.35 grains, theoretically,	1.429 grains,
Of ammonium bromide	1.80   "       "	1.78   "
Of cadmium bromide	1.005   "       "	.885   "
Of zinc bromide	1.43   "       "	1.59   "

The cadmium salt, he states, was not anhydrous, therefore this may account for one discrepancy; the potassium



and zinc point to the presence of oxide, whilst the ammonium seems to indicate the presence of free halogen. Be this as it may, a careful experimenter has found these discrepancies.

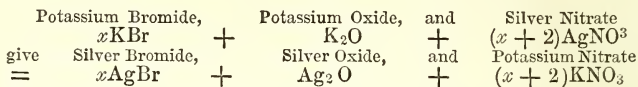
Let us see how potassium bromide may be contaminated in its preparation. We find that the mother liquor from the sea water brine is treated with chlorine, and that this takes the place of the bromine in combination with the magnesium; the yellow liquid is agitated with ether, which takes up the bromine, and this ethereal solution is treated with potash in solution. The bromine forms the bromate and bromide of the alkali, and when the alkali is nearly saturated, it is decanted off and further treated. Now, from what we have said before, it is more than probable that the bromide is contaminated with the alkali, however well it may be separated: the traces of alkali may even be so small as to be undetected by litmus paper.

Again, the bromides of the alkaline metals are prepared by acting on the alkalies with an excess of bromine, a similar reaction to that above taking place. The bromate is decomposed by ignition, and this heating alone tends to decompose the bromide, in which case we should have the oxide of the alkali left behind. In good preparations it would be excessively small, but still sufficient, for the purpose we shall indicate presently.

The bromides of the metals may be similarly contaminated. Take zinc as an example; the metal is easily oxidized, and the zinc oxide is soluble in zinc bromide, as it is in the chloride. In all these cases, then, it is possible we may have traces of oxide with the bromide. Again, there are some metals which form two bromides, as that of copper; and experience shows that it is very hard to get the compound fully saturated with bromine without having part of it in the less saturated state.

If such bromides, contaminated with the oxide, or containing the lower combination of bromine, be brought in contact with silver nitrate, we shall have two separate

reactions to consider. In the case of the oxide contamination, when silver nitrate is in excess, we shall have—



Or, besides the silver bromide, we shall have silver oxide formed.

We have seen that we may have oxides and sub-bromides contaminating the bromides, and in a similar way we may have oxides and sub-chlorides contaminating the chloride. In a communication to the *Philosophical Magazine*, which was reprinted in the photographic journals, the writer showed that it was possible to develop an image on a film never exposed to light, but which was in contact with a film (during the operation of development) on which an invisible image had been impressed. The explanation there offered seems every way to meet the requirements of the case, which is, that where a nucleus, if it may so be termed, exists, there the silver from the adjacent bromide during development will be deposited in preference to any other part of the film. Such a nucleus is found in the silver sub-bromide or sub-chloride obtained by exposing a plate to light. However produced, we may assume it will act in a similar manner.

The case of the oxide is not so clear; but a little experiment will throw light on it. Prepare silver oxide as an emulsion in collodion; dissolve (say) 6 grains of silver nitrate in an ounce of plain collodion, and add to it two grains of potash in alcohol. This will give an emulsion of oxide of silver. Now wash it, treating it as a washed emulsion, and add a drachm of it to an ounce of a washed emulsion which works perfectly free from fog; coat a plate, and develop it. It will be found that inevitable fog is produced. In this case the silver oxide (presumably partially reduced to the metallic state, since the oxide is an unstable compound) acts as

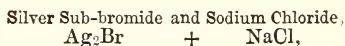


the nucleus on which the silver bromide is reduced to the metallic state by the alkaline developer.

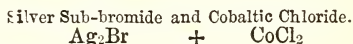
It must be borne in mind that the invisible image must necessarily be composed of very minute particles of the altered silver salt. If, then, such a small number of such particles distributed over a film are sufficiently powerful to form nuclei for the development of the image, the same minute quantity of oxide, or chemically produced subhaloid of silver, might be capable of producing the same results. The above, then, seems to be the explanation of fog in emulsion plates. Now as to the remedies.

It is well known that when we have an excess of soluble haloid, freedom from fog is secured. In some experiments we carried out, we found that silver bromide is formed before any other silver compound, except the iodide, when the sensitive salt is formed from haloid salts, and not from the halogens themselves. Thus, if potassium bromide be contaminated with potash, we shall have both silver bromide and silver oxide formed, if an excess of silver nitrate be added; but if there be a defect of the nitrate there will not be a trace of silver oxide, but only silver bromide. Again, if we take bromide of copper, which is usually contaminated with the sub-bromide, as already stated, it will be found that the bromide is all utilized before the sub-bromide is attacked at all; and if, in addition to the bromide, we have a metallic chloride present, which may be contaminated with sub-chloride, the order in which they will combine with the silver nitrate is: bromide, chloride, sub-bromide, sub-chloride. Thus, if there be only sufficient silver nitrate added to an emulsion to combine with the two first on the list, the other two will be left in the emulsion as harmless compounds. The method of eliminating fog from the finished emulsion in which there is *at first* an excess of silver nitrate is thus easy to guess, and we have the theoretical explanation of Major Russell's statement that a little soluble bromide must be left in the film when

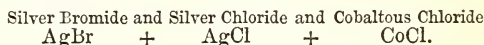
silver bromide is formed by the bath in the usual way. It may be remarked, parenthetically, that whether the image be developed by the alkaline or acid method, the same result must hold good. Supposing we have a washed emulsion which contains bromide, sub-bromide, and oxide of silver, and also a very slight excess of silver nitrate. The addition of certain metallic chlorides or of hydrochloric acid will at once convert the sub-bromide and oxide into the chloride of silver, leaving harmless compounds behind. The metallic chlorides which are of use are those which readily part with chlorine, and which, therefore, preferably form more than one chloride, such as gold, copper, cobalt, platinum, &c. When other chlorides, such as of the alkalis, are employed, the needful substitution may not take place, because the affinity of the alkali for the chlorine is greater than for the sub-bromide; and therefore the elimination of the sub-bromide is not effected. Thus, if all the silver nitrate in original excess be converted into silver chloride, we have the silver sub-bromide to get rid of. Now, supposing we are using sodium chloride as a corrective, then we should have



which can form no new saturated silver compound, since an atom of metallic silver, sodium, bromide, or chlorine cannot be left in a free state; but if we use (say) cobalt chloride, we have—



which can form—



The  $\text{CoCl}$ , or sub-chloride of cobalt, is harmless, and can be washed out of the film.

It will, therefore, be seen how it is that addition of these chlorides to a washed emulsion will give freedom from fog.

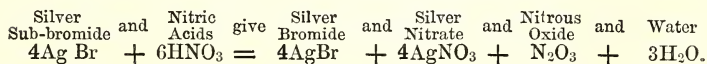
Secondly, if an excess of silver nitrate be used, it is

evident that something else besides a mere chloride will be required, since the sub-salts and oxides would be formed. This we find in the employment of an acid, or of a halogen itself, or both together, added to the emulsion, to be most rapidly effective. Whatever is used is best added to the soluble salts before the silver nitrate is added.

Suppose nitric acid alone be employed, then any oxide or carbonate will immediately be attacked, as also any of the sub-bromides—such as of copper. Again, if aqua-regia be employed, we know that chlorine is evolved in an extremely nascent state, and that this would attack either oxide or sub-bromide, fully saturating the unsatisfied atom in the latter. If, now, silver nitrate be added, silver bromide and chloride would result with some compounds (perhaps such as the chlorate), which would be as inert as producers of fog as the silver nitrate itself.

If a halogen be employed without any acid, the same result would occur. Thus, suppose we had as impurities an oxide and a sub-bromide, and that we added a solution of bromine to it, we should get the oxide changed to a bromide and bromate (the latter salt of which is experimentally proved to be inert), and sub-bromide changed to a bromide.

If the halogen be added last, when there is an excess of silver, it is probable that until all the latter is converted it will exert no unfogging action; but if an acid, such as nitric acid, be added, it will exert its proper influence, though slowly; for it will convert any oxide or compounds of the oxide into nitrate, and from the silver sub-bromide dissolve away the loose atom of silver, converting the sub-bromide into bromide and nitrate. Thus—



Or, at all events, a fresh combination will be made, which is unacted upon by the developer.

There is also a method of eliminating fog from collo-

dion dry plates when coated, without doctoring the emulsion at all. This need not apply only to washed emulsions, but it can be effected during the washing of the plates prepared by the unwashed emulsion. In addition to the elimination by the acids, and by the metals forming two bromides or chlorides, we can further effect it by using a solution of potassium bichromate,\* permanganate of potash, or peroxide of hydrogen, and other oxidizing agents, such as ferric-sulphate and ferric-oxalate. The reason of this seems to be due to oxidation, or to the direct formation of a new product; the writer is still engaged in experiments on the subject. It may be, in the first case, that a minute quantity of silver bichromate is formed by the oxide, or that the free silver atom of the sub-bromide is oxidized, and then formed into silver bichromate; with the second, it may be that the manganese salt is substituted for the silver salt, and is inert; and in the next two cases it may be that the silver salt is per-oxidized, and forms an oxy-bromide, which is unaffected by the developer. This seems probable, since ozone has the same effect on the fog.

It may not be uninteresting to note an experiment which throws some light upon this point, though it is not conclusive. If a plate be coated with collodion emulsion, and be allowed to thoroughly darken in the daylight, and then drops of the above oxidizing agents be placed on different parts of the film, and allowed to act for a few minutes, it will be found, after washing, that on these spots the colour and appearance of the film will remain unaltered. (Where the manganese has been, the film is slightly brown.) Now, if the film be treated with sodium hyposulphite, the parts where all have been will become transparent, showing that everything except the collodion has been dissolved away, whilst on the rest of the plate there will remain a delicate layer of metallic silver. This shows that the loose atom of metallic silver attached to the sub-bromide has

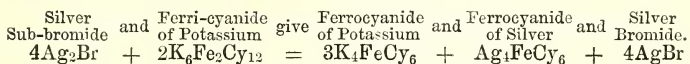
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\* This can be used with gelatine emulsions.

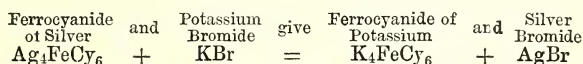
been converted into a salt soluble in hyposulphite of sodium.

Be the theory what it may, the treatment holds good. Perhaps with collodion plates the application of nitric acid is the safest, where possible, but to that we shall refer later on.

Dr. Eder has also shown that potassium ferri-cyanide and potassium bromide will cause the same result. The ferri-cyanide acts as follows:—



The potassium bromide converts the ferro-cyanide of silver into bromide, and ferro-cyanide of potassium is formed. Thus—



From the foregoing it will be seen that fog may be produced by inorganic matter present with the silver salt; and further on it will be seen that it may be produced during development and in emulsification. Regarding this last point there is more to be said in regard to gelatine emulsion, and which will be found more fully treated of later on. Suffice it to say that gelatine itself, when decomposed to any extent, has an alkaline reaction, ammonia being one of the products, and that this will reduce the silver bromide held in suspension in it, unless means be taken to overcome the effect of the alkalinity, or to neutralize the alkalinity. In other words, decomposing gelatine is a feeble developer (or reducer of the silver salt), and may cause fog. The fog caused by the reduction of the bromide to the metallic state is much more difficult to treat than any other, for the mere conversion of the metallic silver into oxide is useless (see page 8). More vigorous treatment is required. This shows that a collodion emulsion is much more readily unfogged than a gelatine one,

since in the former the reduction of the silver salt to the metallic state rarely, if ever, occurs. With collodion the danger is minimized, and acidity rather than alkalinity is to be apprehended. <sup>A</sup><sub>1</sub>

With gelatine plates it is inadmissible to use any substance which may attack the gelatine; thus the application of acids is not to be thought of, nor hydroxyl, nor permanganate of potash. Chloride of copper may be employed, but the safest plan is to use either bichromate of potash or the ferricyanide of potassium with the bromide of potassium; but to this we shall refer at greater length in the practical part of the work.



## CHAPTER II.

### ALKALINE DEVELOPMENT.

It will be noticed that all emulsion plates are developed either by alkaline development, or by ferrous oxalate development, and we propose to consider these two developers from their theoretical point of view. It may be said, first of all, that iodide is not amenable to alkaline development, except under conditions which render it useless to attempt ; the bromide and chloride are amenable to it.

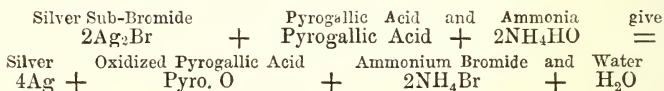
An alkaline developer consists of a strong absorbent of oxygen, an alkali, and a soluble bromide or chloride. The two first are the only two which are essential for the reduction of a salt of silver to the metallic state. Thus, if we take precipitated bromide of silver\* and add to it a solution of pyrogallie acid and ammonia, we shall find that it is rapidly reduced to the metallic state. If, however, we precipitate the silver bromide in the dark, and add to the developing solutions a little bromide of potassium, we find that the mass is reduced more slowly, the

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\* Precipitated by dissolving a little bromide of potassium in water, and adding to it silver nitrate, and then washing.

soluble bromide acting as a retarder to the reduction. If we have a film which has been exposed to a camera image, and develop by the unretarded solution, we shall find a reduction all over the surface; whereas if we use one with the retarder in, we shall find that with it the image develops properly; in other words, the alkaline developer has a tendency to act on the sub-bromide more than on the silver bromide which has been unacted upon by light. During the operation of the reduction of the silver bromide or sub-bromide to the metallic state we have an alteration in the developing solution, the pyrogallie acid becomes oxidized, and part of the alkali enters into combination with the eliminated bromine.

The following equation gives an idea of what will take place, though it is not strictly accurate in a chemical point of view.

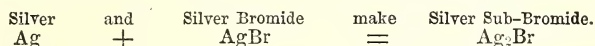


The whole of the action depends upon the affinity for oxygen of the oxygen absorbent. The stronger its affinity for oxygen, the greater the energy of development. The energy of this affinity is checked by a soluble bromide; why this is, is a moot point at present, and deserves rigorous investigation. It is quite certain, however, that by checking its affinity, not only is it less liable to reduce the unaltered bromide, but that it also reduces more tardily the sub-bromide. An absorbent of oxygen, which is capable of reducing the sub-bromide alone at the first shock without reducing the bromide, must be a better agent to use than pyrogallie acid, which requires such a retarder. Such an oxygen absorbent has been found by the writer in hydrokinone, which, under ordinary circumstances, has no tendency to reduce the silver bromide, and it has a greater affinity for oxygen than any known organic



substance. Unfortunately, its value is, as a developer, diminished, owing to its high price.

An alkaline developer is one, then, which reduces the silver sub-bromide to the metallic state, and leaves the silver bromide intact. From what we have said it is evident that silver sub-bromide on an exposed plate must exist in the minutest quantity—in fact, be indistinguishable by ordinary chemical analysis. How comes it, then, that a visible image can be developed at all, since the reduced silver would be even more invisible than the sub-bromide? Experiment teaches us that the bromide of silver cannot exist in close contact with freshly-formed metallic silver. Hence *immediately* metallic silver is formed by the developer, the molecules of sub-bromide in contact with it become sub-bromide. Thus



The freshly-formed sub-bromide is in its turn attacked, and reduced by the developer to the metallic state, and thus the image is gradually built up in metallic silver.

From chemical analogy it may be assumed that the attractive force of the particles altered by light is most vigorous when freshly formed, and that metallic silver also has the same energy of attraction when it is freshly deposited, though it seems probable that in development there is a state in which the sensitive salt can be placed in which it loses its power of attraction in a great measure. With the weak alkaline developer the silver is reduced but slowly from the bromide, and hence it becomes less “nascent,” if we may use the term, than it is when it is rapidly reduced, and when the next particle to it is also rapidly reduced and ready to bind itself to the silver just deposited. Slow deposition of silver is also not conducive to density (as we know by experience when silvering mirrors), and this alone points to the advantage of an energetic developer. Again, from chemical

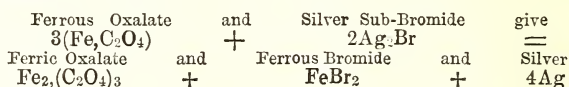
analysis of the developer after it has been used, it is found that a weakly alkaline solution is only capable of reducing a small amount of the bromide compared with a concentrated solution.

It will be noticed that the alkaline developer is nothing more nor less than a silvering solution *minus* the silver, as used for silvering mirrors, the pyrogallie acid taking the place of grape sugar or sugar of milk. The reduction of the bromide to the metallic state is effected in the same way that the reduction of the ammoniacal solution of silver is effected.

It will be observed, that various formulæ are given for alkaline development; in one ferro-cyanide of potassium plays a part, and in another sulphite of soda. The value of both these appears to be that they oxidize with the pyrogallie acid; whether in the absolute act of development, or merely by absorption of oxygen from the air, is undecided. In any case, the longer the pyrogallie acid remains unoxidized, the more effectual should be the development.

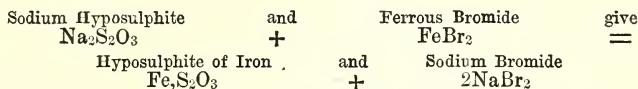
The hydrosulphite developer may be classed amongst the alkaline developers.

We next have to consider the ferrous oxalate developer, and it matters but little, as regards theoretical considerations, as to which way it is formed. It will be seen by the formula given later that the ferrous oxalate developer is in reality a solution of ferrous oxalate, in neutral potassium oxalate. The latter salt exercises no developing action, but is rather a retarder to development than otherwise. We have therefore only to consider the action of ferrous oxalate on silver sub-bromide, and it may be expressed as follows:—



By which it will be seen that a metallic bromide is formed, together with ferric oxalate.

Now, as has already been pointed out, ferric oxalate destroys the developable image (see page 12), hence it is a retarder. Ferrous bromide is also a greater retarder of development than the potassium bromide. Experience has shown the writer that the addition of a small quantity of hyposulphite makes development much more rapid, and that a gelatine plate requires less exposure with it. Let us trace what happens first as regards the ferrous bromide formed:—



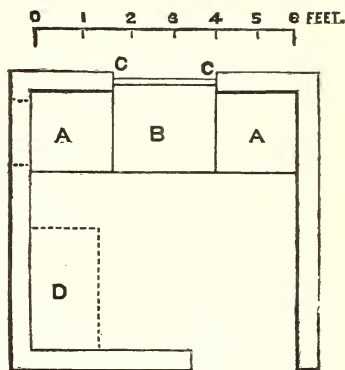
Whence it will be seen that the extra retarding influence of the ferrous bromide vanishes, and the milder retarding sodium bromide is formed. Again, if we trace what will happen when sodium hyposulphite is added to ferric oxalate, we shall find that ferrous hyposulphite and oxalate are formed, and also a sodium oxalate. Dr. Vogel believes that the good effect of the hyposulphite is due to the hyposulphite of iron formed. We ourselves, at the present moment, are not inclined to hold to this explanation. It seems almost more likely that the destruction of the ferric salt immediately on its formation is one cause of the acceleration.

## CHAPTER III.

### DARK ROOM AND ITS FITTINGS.

WE have thought it may be advantageous to give a slight outline on the requirements of the dark room and its fittings. The size of the dark room may, of course, vary, but it may be remarked that a place six feet square is a space large enough in which to work comfortably, but then the arrangement of the room must be adapted to it.

A sample of an arrangement is given in the figure.



*Fig. 2.*

B is the sink ; AA are two working tables. On the left, over A, may be placed a glass shelf, running along the

left wall towards the drying cupboard, D. The right-hand table, A, may be used for the developing bottles and apparatus. The door of the dark room should open outwards, if possible, and be covered by a curtain, which depends on to the ground, thus shutting out all light which would otherwise get through the chink between the door and the floor. Too many precautions to exclude white light cannot be taken, since gelatino-bromide, if it is to take the place of collodion, should be extremely sensitive to it, however feeble it may be.

*Water Arrangements.*—It is always useful to have water laid on to a dark room, but in many cases it is impossible; in that case we recommend that a two-gallon jar be placed some three feet about A (fig.) on the right hand, a hole being bored about two inches from the bottom. A cork with a pierced hole, in which is passed a small piece of glass tubing, should fill up this orifice, and on the glass tube should be drawn a piece of black india-rubber tubing of a convenient length, to which an American clip should be attached. If a hole be bored slantingly through the clip so that the india-rubber tube, when passed through it, comes to the termination of the jaws of the clip, this arrangement, which was first described to us by Mr. England, will answer better than more elaborate contrivances. When water is laid on from the main, a rose is a very desirable adjunct to the tap, since it gives a jet which has no force, and which is like a shower or spray.

*Drying-Cupboards.*—The principles on which a drying-box should be made should be apparent, though in many forms they are neglected. The first principle which should be carried out is that the air passing through it should be capable of taking up moisture. It very often happens that the air which, in some contrivances, is passed through the drying-box is nearly saturated with moisture, hence it can take up but very little more, and plates dry slowly. How, then, can it be made to absorb more? It may be done by causing it to

bubble through sulphuric acid, or by passing it through dry chloride of calcium; but in order for this to be effective, the drying-box must not only be light-tight, but also air-tight, since the air would find its way immediately through any small chink or cranny sooner than force its way through these obstructions. A better mode is to warm the air, since it is well known that warm air will take up more moisture than cooler air, and it is on this principle that some efficient drying-boxes are constructed.

A good type, and an excellent one, too, is that shown in fig. 3. It is Mr. England's plan, and if constructed as in the sketch would take any plates up to 12 by 12.

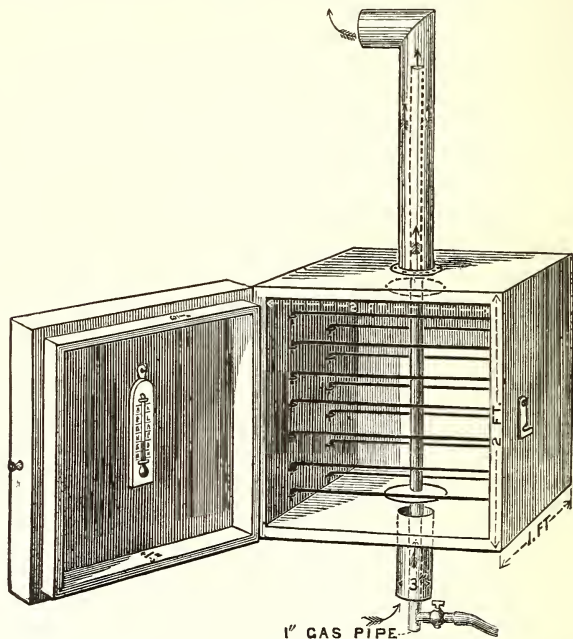


Fig. 3.

A box is made of the dimensions given, and one side



is hinged, and opens as shown. This side has a fillet placed round it, so that on shutting up no light can enter the interior of the box. Through the centre of the box runs a gas pipe, at the bottom of which is inserted a small tube closed at the end, and on the side of which is pierced a small hole. To this hole gas is led, and a very small jet is lighted in the gas pipe. At the bottom of the box, and at the top, are two holes of about three to four inches diameter, and above two tin tubes, some twelve inches long, are fitted into these tubes as shown in the diagram. It will be noticed that the gas piping passes through the centre of these two tubes. Round the gas pipes are fitted two discs of blackened card or tin, one of which is placed two inches above the bottom hole, and the other the same distance from the top hole. These prevent light striking down the tin tube into the box. The plates, when set, are laid on pairs of wires stretched across the box, as shown in the diagram, and a box of the above dimensions may take from half to one dozen plates on each side of the central pipe.

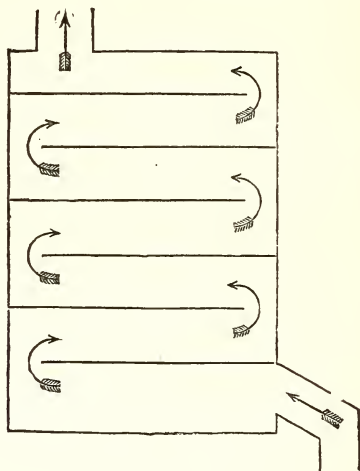
Plates dried in such a drying-box are ready for use four or five hours after coating. A small thermometer should be hung on the cupboard door, to enable the temperature to be noted.

The rationale of this fairly rapid drying is that the gas piping gets heated, warms the air in contact with it, which ascends through the top tin tube, and a current of fresh air comes up through the bottom one. A constant change of air, more than a very dry or hot air, is the object to be attained.

We are in duty bound not only to give its excellencies, but also to point out any defects. In hot weather we have found that plates dried very close to the central pipe are apt to run; the heat is communicated to the iron wires, and the glass takes it up, and the gelatine is apt to melt when the plate touches the wires. This is evidently due to conduction, and we believe that it is better to have a non-

conducting medium in contact with the glass. Small loose cylinders, about half-an-inch long, of pipe-clay, can be readily baked and slipped over the iron bars, and each end of the plate supported by them. For summer weather, when the air is, as a rule, dry, it is a good plan to have a small gas jet placed just above the box in the iron gas tube. This heats the air in the zinc tube, and a draught is created through the box; by this means the air is not above the summer temperature, and is not so quick-drying.

The plan recommended by Dr. Van Monckhoven is one which has long been in use in England, but he has described it as follows:—“The drying-box (fig. 4) is easily



*Fig. 4.*

made, and consists of a box of thick wood, on the top of which is a zinc pipe to connect it with a chimney. At the bottom is another pipe, but with an elbow to prevent light from entering. Horizontal shelves are placed in the interior, so that the current of air obtained by the draught in the chimney goes over each, one after the other. This



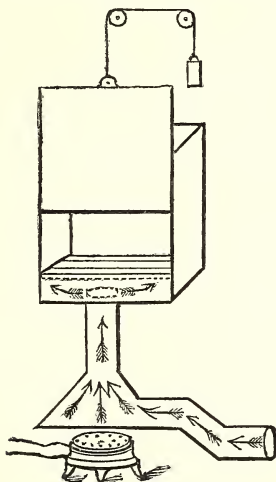
box ought to be placed in a warm and very dark room. As to the necessity of warmth in the room, we demur. It is not necessary if arrangements be made for burning a gas jet in the top tube, so as to create a draught.

Mr. A. Cowan has also described in the *Photographic Almanac* a drying box for dry plates which is essentially correct in principle, and no doubt answers well. He says:

“It often happens in very damp weather that gelatine negatives refuse to dry for hours, and even when flooded with spirit take a considerable time.

“To those who do not possess a good drying cupboard the following is offered as a thoroughly efficient substitute, which anyone can make for himself with a little help from the blacksmith.

“The annexed diagram will explain itself. The box



*Fig. 5.*

may be of any form most convenient, but the more shallow the better. The one in actual use stands on an ordinary work-bench, and the gas-burner, and iron cone, &c., on

the floor, enclosed with a few bricks piled up to keep in the heat and protect any woodwork. A very good proportion for the cupboard is thirty inches high, thirty inches wide, and ten inches deep from back to front. The front is closed up at the lower part about six inches, and a sliding door running in grooves closes the upper part all but about half an inch at the top, a balance weight over a pulley supporting it in any position required. This is found a much better way than having doors opening on hinges, for various reasons.

“The current of warm air is conveyed in at the bottom through a three-inch circular opening, the iron stove-pipe arrangement being screwed on underneath. Above the opening, at a little distance, is supported a thin shelf of wood about an inch smaller all round than the inside of the box, which acts as a diffuser, and stops the current of hot air from rushing up in one spot. Above this, at any convenient height, two bars are fixed to carry the feet of the drying rack containing the plates. It will be found that plates will dry without running at a very considerably higher temperature than that at which gelatine melts if the heated air be kept in continual motion.”

## CHAPTER IV.

### ILLUMINATION OF THE DARK ROOM.

IN all emulsion processes, whether collodion or gelatine, great precautions have to be taken as to the light in which the plates are prepared, since they are necessarily exposed to its action for some considerable time. There are many persons who attempt to prepare emulsions who fail, and the failure may often be traced to the improper lighting of the dark room. For development, a light which would slightly fog a plate during preparation may be used, since it is not necessary that it should be exposed to its action more than a second or two, which would not be sufficient exposure to cause any perceptible fog. When once development begins, the ingress of more actinic light has but little effect, since there is sufficient bromide used in the development, with the alkaline development, to render the silver salt insensitive; or, if ferrous oxalate be employed, the solution itself is of a colour which effectually cuts off all light that would rapidly harm the image. We have made these remarks, not to discourage the idea that a perfectly safe light should be used, but to show that when such cannot be procured, as on tour, it is possible to develop plates without any danger. It is necessary, first of all, to know what kind of plates are to be prepared,

and worked, before deciding what light to admit to the dark room. For instance, with collodio-bromide, an orange light will be sufficient; but with gelatine plates containing pure bromide, a ruby light in which there is no green is absolutely essential. It is safe, however, in all cases, to have a red light, and we recommend it for general adoption, since every kind of plate can be worked in it.

One maxim to remember is, that if the quality of the light be correct, the quantity may be unlimited. To make this more clear, a diagram from another work\* is reproduced, from which a notion can be obtained as to the light to which different plates are sensitive, and the media which may be accepted to cut off that light.

No. 1 may be omitted from consideration, since it is sensitive to all rays, and no filtered daylight is admissible where it is employed; but Nos. 2, 3, and 4 should be studied. When a streak of white light is passed through a prism it is spread out into its component colours, and in 14 they are represented as white. The black portions in 2, 3, and 4 of the diagram show the rays of light in every case which do not affect a sensitive plate. The white and half-tints represent, as approximately as can be shown in a wood-cut, the relative sensitiveness of the plates to the different rays forming white light; the degree of sensitiveness being indicated by the degree of whiteness. It will be noticed that the gelatino-bromide and collodio-bromide plates are sensitive to the confines of the red, and some specimens of the former are also sensitive well into the red, whilst the bromo-iodide is only sensitive to the confines of the yellow. Next we need only turn our attention to Nos. 5, 6, 7, 8, 9, 10, and 12. In these are shown the rays of light which pass through different coloured glasses and dyes.

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\* "Instruction in Photography" (Piper and Carter), 4th edition.

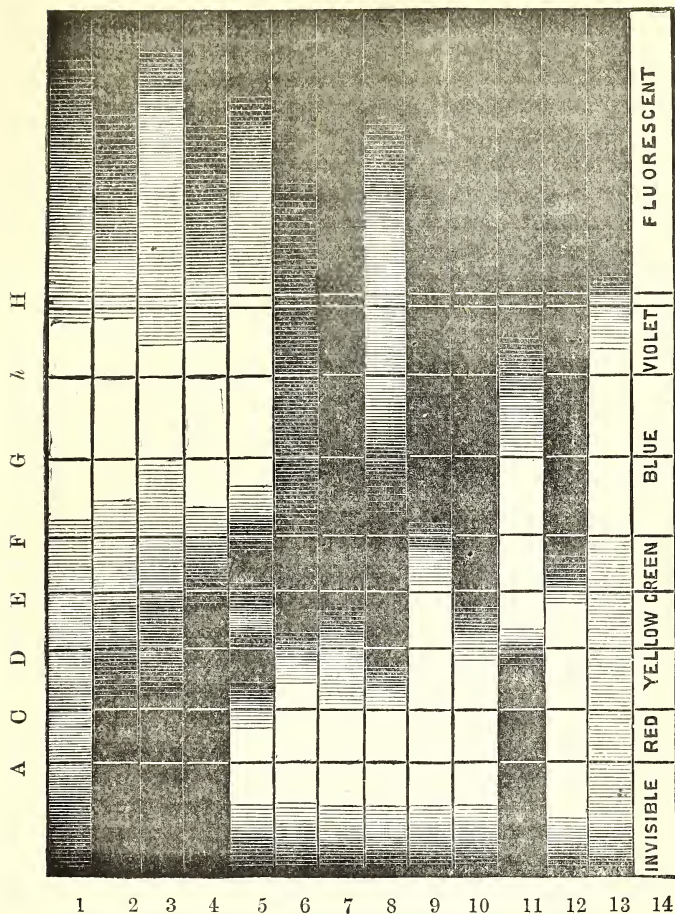


Fig. 6.

1. Special collodio-bromide.
2. Gelatino-bromide.
3. Collodio-bromide.
4. Bromo-iodide.
5. Cobalt glass.
6. Ruby glass.

7. Chrysoidine.
8. Magenta.
9. Flashed orange.
10. Stained red glass.
11. Bottle-green glass.
12. Aurine.

13. Quinine.



Ruby glass would be a perfect protection for nearly every plate were it not that a certain amount of blue light passes through one thickness of it. When two thicknesses are used the blue is imperceptible. By the use of a combination, orange glass and ruby, or stained red glass and ruby, the light allowed to pass through is such as will not affect most of the sensitive plates, since the orange or stained red entirely cuts off the blue which may permeate the ruby glass. Several persons with whom the writer has come in contact have told him that they prepare plates so sensitive to the red that the light passing through any number of thicknesses of ruby glass proves an ineffectual protection to the plates they prepare. Unless ruby glass were added till total darkness supervened, there is nothing to surprise us in this statement, as the red light which filters through three or four thicknesses of ruby glass has the same quality as that which filters through two thicknesses. What they really express is that they prepare plates which are in reality sensitive to red light. When this is the case, the development and preparation of such an emulsion become a nuisance, and are probably more of a scientific than of a practical value, since the same sensitiveness can be produced without any liability to veiling of the image through the impact of light of such low refrangibility on the plate. For an ordinary dark room we recommend that, if a north light be obtainable for the window, one thickness of ruby and one of stained red or orange glass be employed. As to dyes, it will be seen that if glass be coated with aurine on one side, and magenta on the other, the same spectral quality will be obtained. If plates very sensitive to the red be prepared, one thickness of cobalt glass and one of stained red will be the best combination to use; but, as we said before, plates requiring such a light by which to develop should not find a place in a photographer's hands. If the sun shine on the window during any part of the day, it is well to have a screen, which can be placed against the window-

frame (it can be hinged from the top, and pulled up as a flap by a small pulley arrangement), covered with orange-coloured paper. This diffuses the light, and renders any chemically active rays which can possibly filter through it less hurtful. It is not always practicable, however, to work by day, and then it becomes necessary to resort to artificial light, and that must be of the same character as the filtered daylight. Now, candle and gas light have not the same amount of blue in them as the light from the sun, hence the screen used for shielding such sources need not be quite so perfect. In our practice we have a common stable lantern fitted up for this purpose. Holes are pierced at the bottom of it for the indraught of air, and holes at the top of the sides for the outdraught. To prevent any light striking the ceiling, we have had a tin cover fitting round the lantern\* at the top, and sloping  $45^{\circ}$  downwards, by which means any light glancing through the holes strikes the shade and is reflected downwards. The glass walls are coated with magenta and aurine dissolved in common shellac varnish. Thomas' ruby varnish answers well. Its colour seems to be due to the combination of the same two dyes

Some dry plate men we know have gas burning close outside a ruby glazed window which opens into an adjoining room, but it is not every one who can have such an arrangement.

For developing plates away from home, we have found that a useful piece of apparatus can be easily made. Take a sheet of cardboard of the size of about 2 feet by 1 foot 6 inches. Lay off from the 2 feet side distances of 6 inches from each corner, and with a penknife cut half through the card in a line parallel to the ends. These will form flaps, which can be folded over to meet in the centre. From the centre portion, and 6 inches from the bottom, mark out a square of 8 inches; cut round three

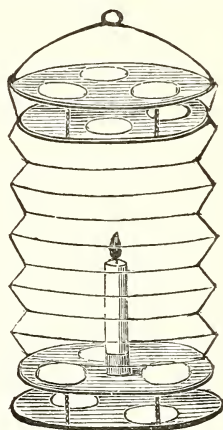
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\* Some lanterns are made with this arrangement.



of the sides, but only half cut through the bottom side, the penknife being applied from the inside of screen. This will allow a square flap to fold downwards towards the outside. On the inside of the opening may be pasted or hung two of orange paper; or a sheet of paper dyed deeply with a mixture of aurine and aniline scarlet may be glued to it. The candle is placed behind the screen, which should stand, supported by the two wings, in front of the operator. A piece of board, or a piece of tin, may rest on the screen, and thus cut off diffused light from the ceiling. We have developed many plates with such a light, and lost none by veiling of the image. When packed for travelling the flaps are folded up, and it can be placed in the portmanteau.

A useful portable lantern is made from a Chinese lantern. We first saw it adapted in Mr. Galton's hand; but Dr. Hermann Fol has given a practical method of its construction in the *PHOTOGRAPHIC NEWS*. He describes it as follows:—"The most portable lantern I make by



*Fig. 7.*

painting over common white paper Chinese lanterns with collodion containing castor oil and fuchsine. The top

and bottom of the lantern are made each of two thin metal plates fastened together by three small chains. Each plate is pieced with holes, and each pair is fastened to the chains so that the holes do not correspond, and half-an-inch remains between the two plates. No white light can then find its way out. The upper pair is, of course, unfixed, and may be lifted out to get access to the candle. This lantern folds up into the smallest possible compass, and when in use perfectly precludes all actinic light without getting hot.

## CHAPTER V.

### COLLODION EMULSIONS.

THE first emulsions of which we shall treat will be the collodion emulsions, for which, at one time or another, a great variety of formulæ have been published. It would be impossible to give all which have from time to time been given in the various photographic publications, but a selection has been made of what the writer conceives to be the most successful; at least, which have proved most successful in his hands.

These may be divided into two classes: one, in which the emulsion is formed in collodion and the plate coated and then washed; the other, in which the same emulsion is dried and washed, and re-dissolved, the plate being coated with the emulsion as required. With the former method, unless the bromide is in excess, the emulsion has to be prepared from time to time as required, and if the bromide be in excess the emulsion works very slowly. With the latter process, where it is washed, the emulsion will keep any time, always supposing no decomposition sets up in the pyroxyline. We have ourselves kept some emulsions of this class seven years which are just as sensitive, if not more sensitive, than when freshly prepared.

*The plain collodion with which the emulsion is to be made*

shall be first dealt with, distinguishing the qualities necessary for the unwashed and for the washed emulsion.

Some emulsion workers have laid it down as an axiom that the pyroxyline for the two processes should differ, while others declare that this is unnecessary. Again, some declare that to gain good density the pyroxyline should contain a percentage of organic matter, presumably to be capable of acting on the silver bromide during development, or by forming some definite compound with silver. Our own experience is, that for securing density, organic matter is unnecessary, though it may improve sensitiveness; and we have found in some instances that density was absolutely impossible to attain where organic matter was present. We shall touch on the question of density of the image further on.

If a preservative be used as a sensitizer, there can be no doubt that a collodion should be used which is as porous as possible, to enable it to surround the particles of the sensitive salt. This porosity has also another advantage, which is, that when the preservative is washed off previous to development, the sensitive salt is immediately accessible to the action of the developer. It is such a collodion that is recommended for dry plates prepared with the aid of the bath, more particularly in the collodio-albumen process, though in this process the sensitive salt is more especially contained in the albumen, and it is therefore necessary that a fair quantity of the latter should be on the plate, which is accomplished by this porosity of the collodion film. For any emulsion process, we consider a horny collodion objectionable, owing to the difficulty that exists in making the developer penetrate through the film. A horny collodion has, however, one advantage in that it acts as a varnish to exclude the air from the sensitive salts enclosed within it. In the following formulæ which are given for the preparation of the pyroxylines, one will produce an ordinary tough film, and the other a fairly porous film, and consequently a rather powdery pyroxyline.

The solvents of the pyroxyline should be as pure as practicable to secure the maximum of sensitiveness, and this has been shown to be the case by that indefatigable experimentalist, Mr. H. Berkeley, in a communication he made to the *British Journal of Photography*. There is, for instance, no doubt that when methylated alcohol is used, there may be a lack of sensitiveness, and even a production of fog. The ordinary methylated ether, however, will be found, as a rule, to be sufficiently pure.

## CHAPTER VI.

### PYROXYLINE.

THE following formulæ for the preparation of the various kinds of pyroxyline will be useful to note. The first is taken from "Instruction in Photography," and is reprinted here as being convenient for reference. "The general directions given are those recommended by Hardwich.

#### *1st Process.*

Take—

Sulphuric acid (1·842) at 15° Cent.	18	fluid ounces.
Nitric acid (1·456)...	...	6    "    "
Water                    ...                    ...	4 $\frac{3}{4}$	"    "

Or,

Sulphuric acid (1·842)	...	18	fluid ounces.
*Nitric acid (1·42)	...	6 $\frac{1}{2}$	"    "
Water                    ...                    ...	...	4 $\frac{1}{4}$	"    "

The water is first poured into a strong glazed porcelain basin, the nitric acid next added, and lastly, the sulphuric acid. The mixture is well stirred with a glass rod. The temperature will now be found to be somewhere about

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\* The nitric acid of the strength given in this formula is cheaper than that of the first, and is a standard strength, hence it is recommended for economy's sake to use it.

190°. It must be allowed to cool to 150°, and this temperature must be maintained on a water-bath. A dozen balls of cotton wool, weighing about thirty grains (which have previously been well washed in carbonate of soda and thoroughly dried), should now be immersed separately in the fluid with the aid of a glass spatula. Each ball should be pressed separately against the side of the basin, till it is evident that the acids have soaked into the fibre. Care must be taken that each one is immersed at once. Failing this, a different chemical combination takes place, and nitrous fumes are given off, and the success of the operation is vitiated. Immersing the dozen balls will take about two minutes. The basin should after this be covered up for about ten minutes.\* At the expiration of this time the whole of the cotton should be taken up between two glass spatulas, and against the sides of the clean porcelain capsule as much of the acids as possible should be squeezed out. The cotton should then be dashed into a large quantity of water, and washed in running, or frequent changes of, water for twenty-four hours. Finally, when it shows no acid reaction to blue litmus paper, it is dried in the sun or on a water-bath.

### *2nd Process.*

Sulphuric acid (1·842)	...	...	6	fluid ounces
<i>Dried</i> nitrate of potash	...	...	3½	ounces (Av.)
Water	...	...	1	fluid ounce
Best cotton wool	...	...	60	grains

Mix the acid and water in a porcelain vessel, then add the nitrate (which has previously been dried on a metal plate to about 250°, and then pulverized) by degrees, stirring with a glass rod until all lumps disappear, and a

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\* This prevents the access of the air to the fluid, and prevents the absorption of oxygen, and consequent formation of the nitrous fumes.



transparent viscous fluid is obtained. This will occupy several minutes.

The whole of the cotton wool must now be separated into balls the size of a walnut, and immersed as stated in the first process, care being taken that the temperature is kept up to  $150^{\circ}$ . The cotton is then left ten minutes, and washed as before. Mr. Hardwich states that the chances of failure in this process "are very slight if the sulphuric acid be sufficiently strong, and the sample of nitrate not too much contaminated with chloride of potassium." If failure occur through the cotton dissolving in the acid, a drachm less water must be used.

In both processes the operation may be conjectured to be successful if the cotton tear easily in the hand, and if the original lumps cannot be easily separated. Should nothing but fragments of the lumps be detected, it is probable (if the acids used have been of the strength given above) that the temperature has been allowed to fall. If dried, the pyroxyline should, when pulled, break up into little bits, and should not resemble the original cotton in texture.

The weight of good pyroxyline should be greater than the original cotton by about 25 per cent.

If the acids used are too strong, the pyroxyline will be much heavier than this percentage, and will make a thick glutinous collodion; whereas, if the acids have been too diluted, it will probably weigh less than the original cotton, and will yield a collodion adhering firmly to the plate, and giving negatives of too great softness: any small particles of dust that may fall on the glass will form transparent marks. The formula given steers between the two extremes. There is a large proportion of sulphuric acid in the above solution of acids, and it is to this that is probably due the tough film which the resulting collodion gives. In fact, the excess of sulphuric acid partially "parchmentizes" the cotton.

The late Mr. G. W. Simpson described a modification

of Hardwich's formula, which has given excellent result in our hands; the mode of procedure is the same as that described above. The following is an extract taken from the PHOTOGRAPHIC NEWS:—"As Hardwich's formula for the manufacture of pyroxyline is given, we may add a caution derived from our own experience with it. In our practice, we found it to contain too large a proportion of water, and our experiments with it issued in something like fifty per cent. of failures, the cotton dissolving almost entirely in the acids. We may add a formula which we have found to give an excellent sample of soluble cotton for emulsion work, the collodion holding the particles of silver salt well in suspension, and giving a homogenous film, adhering well to the glass. The formula we subjoin has the advantage that the acids are readily obtainable in commerce of the strength we mention, and are consequently cheap. Six measured parts of sulphuric acid 1·840 (ordinary commercial oil of vitriol will serve), and four measured parts of nitric acid 1·360. This is the strength of acid commonly sold as a pure nitric acid. In three measured ounces of the mixed acids, one drachm of cotton wool should be immersed at a temperature of 150° Fah., using a water bath to maintain that temperature for ten minutes, when the cotton should be removed and washed at once in a large quantity of water. India-rubber gauntlets should always be used when making pyroxyline."

In the next formulæ the proportion of sulphuric acid is diminished, and in consequence we get a pyroxyline which is, if anything, deficient in tenacity. For dry plate processes with the bath, however, it is excellent, and will be found of great use in emulsion processes in which a preservative is used. The formulæ are those given by Warnerke in a communication to the Photographic Society of Great Britain made in 1876.

His *modus operandi*, based on a communication made to him by Colonel Stuart Wortley, is the following:—

100 grains of the finest cotton-wool are put into a porcelain jar, and 30 grains of gelatine dissolved in the smallest amount of hot water are added. By pressing it with a wooden stick, all the cotton will be uniformly impregnated. It is subsequently very thoroughly dried before the fire.

Nitric acid (sp. gr. 1.450)...	...	4	fluid ounces
Water	... ..	12½	drachms
Sulphuric acid (sp. gr. 1.840)	...	6	fluid ounces

are mixed in the order named. An arrangement is provided to keep the temperature of the mixture uniformly at 158° Fahr. The dried gelatinized cotton, weighing now about 130 grains, is immersed in the mixed acids, and left in twenty minutes. After the lapse of this time the acids are pressed out, and the pyroxyline quickly transferred to a large vessel of water. Washing and drying follow. Colonel Stuart Wortley recommended also a second mode. Gelatine, instead of being added to the cotton, is dissolved in the water figuring in the formula of the acids, and ordinary dry cotton immersed in the mixture of gelatinized acids.

Mr. Warnerke states that before washing the gelatinized emulsion a remarkable increase of intensity and sensitiveness is obtained. After washing, the difference is less striking, but still sufficiently marked to prove the new pyroxyline to be a very decided improvement.

Mr. Warnerke states that pyroxyline giving extraordinary density can be prepared from the raw hemp. Colloid from hemp-pyroxyline is red in colour, and very fluid; but the insoluble deposit is very considerable; it also requires stronger acids. It is worth remarking that the strength of acids must vary with different samples of fibres, even in the case of different cottons. A very good pyroxyline can be prepared from Whatman's hand-made paper, instead of the cotton in the above formula, which, being sized with gelatine, offers a ready-made material, suitable for making gelatinized pyroxyline."

The great difficulty in this formula is the easy solubility of the cotton at the high temperature. A reduction in the amount of water will prevent this. *Pyroxyline from ordinary cotton can be prepared by the same formula,* and gives a powdery film. The writer disagrees with Mr. Warnerke as to the desirability of this state of the film for washed emulsion when used on rigid supports, such as glass, but the limpidity given by it to the collodion is very desirable in the case of a flexible support, such as that with which Mr. Warnerke's name is associated.

Mr. J. Traill Taylor gave an excellent description of the method to be adopted for making any pyroxyline suitable for emulsion. He says :

“Pyroxyline possessing the requisite qualities is by no means so easily obtained as the ordinary sort. Precipitated pyroxyline forms at once, if properly made, even from the cheapest materials, not only a perfect substitute for the high-priced samples usually employed, but for some purposes gives an absolutely superior result.

“We commenced with a sample of pyroxyline which is sold at 16s. the pound; it is very soluble, and gives little or no residue, but is of little use for emulsion work. Of this 400 grains were dissolved in a mixture of 10 ounces of methylated ether, s.g. .730, and 10 ounces of ordinary methylated spirit, retailed at 5s. a gallon. The resulting collodion, after standing for a couple of days, though very thick, as might be expected, was tolerably clear, except for the presence of a few floating specks and particles of dust, which were removed by passing it through muslin. This was poured into cold water, and the precipitate, when washed and thoroughly dried, weighed 368 grains, or exactly 8 per cent. less than the original cotton.”

After stating that it is a wrong plan to pursue to pour the collodion gently on the water, the writer continues :

“The proper course to follow, as laid down by M. Chardon, is just the reverse of this; the collodion is

poured into the water in a thin stream—preferably from a height—and is stirred vigorously during the time of pouring, and for a minute or two afterwards. By this means it is broken up into innumerable drops, each of which, immediately it comes into contact with the water, is converted into a distinct spongy mass or flock, being deprived almost instantaneously of its ether and alcohol. The stirring is continued as long as the mass exhibits any cohesive tendency, and when it feels harsh and firm to the touch it may be known that the removal of the solvents is complete. The water is then changed, the cotton passed through a cloth, and dried.”

Mr. J. T. Taylor further says:—“Except in physical conditions, we cannot find, with a given sample of cotton, that it is of much importance whether the precipitation is performed in hot or cold water.”

In order to avoid waste in washing and drying, it will be found convenient to employ a conical bag fixed upon a hoop of thin cane. When the precipitation is complete, the whole of the contents of the vessel are transferred to the washing bag, and after passing two or three pints of water through to remove the last traces of ether and alcohol, the mass of cotton is squeezed as dry as possible, and may then be removed as a lump; it is then broken down with the fingers or a spatula upon a clean porcelain dish, and dried at a gentle heat on a water bath. When quite dry, it should present the appearance of light flakes of pure white, and easily reduced to powder. It dissolves as rapidly as ordinary pyroxyline, and if carefully prepared gives at once a perfectly bright solution of a faint yellow tinge. It gives upon the glass a hard, smooth film, non-contractile, and yet differing totally from the so-called powdery films commonly spoken of in connection with dry plates.

In the same article a reference is made to M. Blondeau's analysis of precipitated cotton, in which it is stated that 8 per cent. of water is taken into combination. This



amount of water, if it exist in the cotton, must alter the structure of the collodion in a marked way.

Be this as it may, precipitated cotton does give a very fine film ; but we are inclined to think that part of the effect is produced by the alcohol being eliminated from it *en masse*, and carrying with it that constituent of the pyroxyline which is soluble in the alcohol. This will be seen to be the case in which a finished emulsion was washed in alcohol ; the resulting film having much resemblance to that of M. Chardon's.

The amateur will probably find it most convenient to purchase ordinary pyroxyline from some respectable dealer, who is a manufacturer of good collodion, instead of making it himself, for of all processes connected with photography, that of making pyroxyline is, perhaps, the most unpleasant and hurtful to the health and clothes. The stains on the latter from nitric acid or sulphuric acid can never be eliminated, unless the acid be immediately neutralized, and sulphuric acid will rapidly eat through any organic texture, unless it be either washed *thoroughly*, or an alkali be applied.

As regards the character of the solvents, there is little to be said in regard to the ether. That of a specific gravity of  $\cdot 730$  is generally employed, and, if it be, an alcohol of low specific gravity should be employed, such as  $\cdot 812$ ; whereas if the ether have a specific gravity of  $\cdot 720$ , a specific gravity of  $\cdot 820$  for the alcohol is allowable.

After the plain collodion (see next page) is mixed, it should be allowed to settle. No matter what pyroxyline be employed, it will invariably be found that there is some flocculent matter, too fine for filtering out, which, if not got rid of, is one great cause of spots on emulsion plates, and therefore every effort should be made to prevent its finding its way into the emulsion. The collodion should, therefore, be allowed to remain undisturbed for a week or two, to allow these fine particles to deposit.

## CHAPTER VII.

### PREPARATION OF AN EMULSION.

It is unnecessary to enter into the history of the emulsion processes ; but it may not be uninteresting to note that the first published formula for a collodio-bromide emulsion was by Messrs. Bolton and Sayce, in September, 1864.

Though not following an historical order, we have thought it best to give the method of preparing an emulsion which can be followed in nearly all modifications of the process ; and to make it clearer, a definite formula has been made use of, giving an emulsion which is very simple and clean working, and though not boasting any extraordinary sensitiveness, is yet more sensitive than any bath dry-plate process with which the writer is acquainted.

The plain collodion\* is made as follows :—

Alcohol .820	...	...	...	10 ounces
Ether .730	...	...	...	20    ,,
Pyroxyline (ordinary)...	...	...	...	400 grains

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\* If the plain collodion supplied by dealers be used, it must be recollected that, as a rule, it contains about 5 grains of pyroxyline to the ounce after the iodizer has been added. The formula may be taken to be as follows:—

Alcohol...	...	...	...	...	20 ounces
Ether ...	...	...	...	...	40    ,,
Pyroxyline	...	...	...	...	400 grains

The bromide and silver must be added *according to the grains of pyroxyline, not according to the amount of solvents in which it is dissolved.*



We will suppose that we are going to prepare an emulsion which will make up to twenty ounces. When it is evaporated, washed, and re-emulsified, each ounce of washed emulsion should contain about 5 grains of pyroxyline, and, therefore, we must take one-fourth of the collodion made up as above (*vide* Note page 45), which will be  $7\frac{1}{2}$  fluid ounces. It is proposed that each fluid ounce of re-dissolved emulsion shall contain about 15 grains of silver bromide. The salt we propose to use is zinc bromide, and we find that about 10 grains of this salt are necessary for this purpose. To our  $7\frac{1}{2}$  ounces of collodion, therefore, we must add at some time or another 200 grains of this salt. Two portions of 100 grains each are weighed out: one is dissolved in the smallest quantity possible of alcohol, and 4 or 5 drops of concentrated nitric acid are added to it to render innocuous any oxide or other impurity that may be present. This is then added to the collodion. The other 100 grains are similarly dissolved, but a larger proportion of nitric acid added, viz., 10 drops. This is kept in a test-tube ready for use. We next require 300 grains of silver nitrate to saturate the zinc-bromide, and to allow 3 grains in excess for each ounce of the concentrated collodion. As this will probably be about 11 ounces by the time the additions are made, 330 grains of silver nitrate (which has previously been pounded up in an agate mortar, or the crystals of which have been crushed with a glass stopper on a thick glass plate) are weighed out. This amount is then placed in a large test-tube, with 5 dr. of water, and warmed: a perfect solution ought to result. Ten drops of nitric acid are next added to it. In another test-tube  $1\frac{1}{2}$  ounce of alcohol ( $\cdot 820$  to  $\cdot 830$ ) are boiled, and poured upon the dissolved silver. The two fluids may not mix at first, but by pouring them from one test-tube to another this is readily accomplished. The collodion is now placed in a glass jar, and a stirring-rod placed ready to hand. It is usually insisted that the subsequent operations should be con-

ducted in the dark room. This exclusion of light is quite unnecessary (as the writer has practically proved), owing to the presence of the nitric acid, which renders the sub-bromide inert as fast as it is formed by the action of light. The test-tube containing the silver is now taken in the left hand, and the stirring-rod in the right, and three-quarters of the silver nitrate solution is poured, drop by drop, into the collodion, which is kept in brisk agitation by the glass rod. The silver solution is then placed on one side, and the dissolved bromide solution taken in the left hand. All the latter is now added drop by drop, and then the remainder of the silver solution in a similar manner. Some of the silver salt is sure to be found crystallized on the edge and sides of the test-tube. This is re-dissolved, as before, in a little water and half an ounce of alcohol, and added with the same precautions. If the above details have been carefully carried out, the colour of a candle or gas-flame, when viewed through the liquid which runs down the inside of the glass jar after agitation, should appear of a deep orange approaching to a ruby tint. When in this condition, it may be judged that it has been rightly prepared. With the glass rod a drop or two of the emulsion should be dropped on to small strips of glass, and examined by daylight for structure, &c. When viewed through a window, the principal part of the light transmitted should be orange. A little potassium *chromate* should be dropped on to the emulsion on the plate, and a bright red colour will show that the silver is in excess, which is what is required in our case. If this colouration be absent, it will indicate that the soluble bromide is in excess, which, in some modifications of the same process, is what may be desired. The emulsion must next be decanted off into a bottle capable of containing at least double the amount of fluid—that is, at least 20 ounces—and it should then be shaken for ten minutes. It may now be put on one side for from sixteen to twenty-four hours, when it will be ready for the next operation.

We will now give a slightly different method for mixing the silver and the soluble bromide, which has been adopted by some people, amongst others by Warnerke, to whom the writer is much indebted for information on various points.

A couple of corks, D and E (fig. 8), which should fit the necks of the bottles A and B, are bored with holes just wide enough to admit a glass tube, C, which has a diameter of bore of about one-eighth of an inch. The whole of the bromide is dissolved in half the amount of collodion used, and placed in the bottle A, which (like B) should have sufficient capacity to hold double the amount of emulsion to be made up ; the cork, D, with the glass rod, C, should

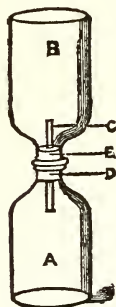


Fig. 8.

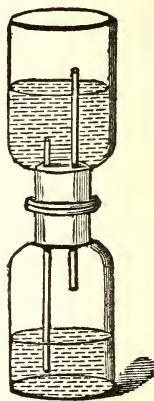


Fig. 9.

next be fitted into it. Into the other bottle, B, the silver nitrate solution is added to the collodion, sufficient alcohol and water being used to keep it in thorough solution. The bored cork, E, is then fitted into the neck, and the far end of the glass tube deftly inserted, and the tops of the bottles brought close together. The hands then grasp the necks, and the contents are shaken up, when a little of B gradually finds its way into A. The positions of the bottles are

then reversed, and a little of the contents of A shaken into B; when each of the bottles seems to contain emulsion equally dense, the whole of one bottle is gradually caused to drop into the other, and by this means a perfect emulsion is obtained. The emulsion may be made even more rapidly by adopting the contrivance shown in fig. 3, in which there are two tubes, one always acting as an inlet for air, whilst through the other the collodion finds a passage. In this case, narrow bored tubes are advisable, certainly not greater than one-eighth of an inch.

Now it has been said that in sixteen to twenty-four hours the emulsion will be ready for pouring out. This statement is true for the particular emulsion described, but it is not necessarily true for emulsions when other soluble bromides are employed. Thus we find that Col. Wortley stated to the Photographic Society of Great Britain, on 14th March, 1876, that the following is the time necessary for emulsions made with the following soluble bromides to ripen :—

Manganese	...	...	...	7½ hours
Cadmium	...	...	...	9 "
Strontium	...	...	...	10 "
Magnesium	...	...	...	10 "
Zinc ...	...	...	...	10½ "
Cerium ...	...	...	...	14 "
Potassium	...	...	...	14 "
Cinchonine	...	...	...	15 "
Sodium...	...	...	...	15¼ "
Calcium	...	...	...	17 "
Ammonium	...	...	...	17½ "
Uranium	...	...	...	17½ "
Barium...	...	...	...	19 "

It will be noticed that Colonel Wortley gives zinc emulsion ten and a-half hours, as the time for attaining the maximum sensitiveness. The discrepancy is probably due to the greater viscosity of the collodion employed in

the one case as compared with the other. The list, however, is useful as showing the comparative times that should be allowed for ripening. We might here leave the emulsion as ready for coating plates after proper dilution, but we will further suppose that it is to be washed, a modification introduced by Mr. W. B. Bolton, one of the originators of the collodio-bromide emulsion process. The first step to be taken is to allow the solvents to evaporate.

*Evaporating the Solvents.*—An emulsion generally may be prepared in the afternoon of one day, well shaken before leaving the laboratory, and on the next day, about noon, the emulsion will be ready for drying. The mode adopted by the writer is as follows:—The emulsion is poured out into a flat dish, to a depth of a quarter of an inch, and placed in a dark room, the temperature of the latter being raised, if possible, to 70°. For the ten ounces of emulsion made, a porcelain dish, about 14 by 12 by three-quarters of an inch deep, is required.

After a short interval it will be found that a skin forms on the surface of the collodion; this is broken up with a glass rod, and a fresh liquid surface given to it. Every half hour the whole of the emulsion is thoroughly well stirred up, till it begins to break into lumps, when it can be left a short time, for the solvents still further to evaporate. It is ready for the first washing when the lumps require a little force to break them up—in other words, when they are about the same consistency as a collodion film before dipping into the bath. The mass is then removed to a glass beaker, and covered with distilled water. At this point we have a good test as to whether the evaporation of the solvents has been continued far enough. If only a few of the lumps rise to the surface, the evaporation has been sufficient; if, on the other hand, the majority float on the surface of the water, it has not been continued long enough. The reason of this tendency of the lumps to rise to the surface is due to the light specific gravity of the ether and alcohol, which,



even with the weight of the solid matter, is not sufficient to counterbalance the specific gravity of the water.

This method of eliminating the solvents is, however, wasteful, and, if preferred, resort may be had to distillation (see Appendix); but this method should not be adopted *unless all acid be omitted* previous to distillation, since boiling an emulsion in its presence produces a very horny film, and nitrous ether is formed. The acid must be applied in the first wash water. Let it be recollected that where the bromide is not in excess, *but where there is an excess of silver nitrate, nitric acid or its equivalent must be added to the emulsion itself, or to the wash-water* at some stage—the time of addition being dependent on the circumstances already explained. *The whole of the operations up to the first washing may be carried on in the light.* In M. Chardon's process, as subsequently given (page 59), it will be seen how this evaporation of the solvents, previous to washing, may be dispensed with. It is hardly worth while to repeat the method here, more particularly when, in some respects, the above is really superior to it; at least, so the writer has found.

For the above quantity of emulsion, 1 drachm of nitric acid, which will be ample to secure freedom from fog, should be dropped into the dish, and distilled water added. After a couple of hours the true washing may commence.

A method which we have found to give still better results, if the acid is omitted from the emulsion, is to wash the pellicle twice or three times in water till nearly all excess of silver is removed, and then to add 2 drachms of hydrochloric acid to the next wash-water (which should not be more than 10 ounces), and then begin to wash *de novo*. Mr. Bedford first recommended this plan. Instead of the hydrochloric acid, a solution of bichromate of potash, 10 grains to the ounce, to which a pinch of common salt has been added, may be substituted. This is an excellent method, since any trace

of bichromate is visible in the wash-water. The pinch of salt prevents the formation of bichromate of silver.

To wash the emulsion it may be placed in a jar or jam pot, and be covered with water where it can stand two or three hours in the dark without detriment, when it should be changed. The way in which the washing can be economically effected, as regards time, is as follows:—A piece of coarse calico which has previously been washed in carbonate of soda, and then well rinsed, and dried, is spread over the top of a second glass jar or large jam pot, and the contents of the first thrown on to it. The calico acts as a strainer, and the solid pellicle is left on it. The calico is next taken up by the sides, and the contents are twisted up in it, and as much as possible of the liquid then wrung out. The calico is untwisted, and a bag formed by tying up the ends, to hold the emulsion, which is shaken up and immersed in fresh distilled water. After a quarter of an hour the wringing operations are again proceeded with, and this process repeated three or four times. The expelled water should now be tested for free silver nitrate by a drop of hydrochloric acid. If it gives more than a slight milkiness, such as is produced by adding silver nitrate to water containing a grain of common salt to the gallon, it must be washed till this maximum is attained.

*Preparing the Pellicle for Re-emulsifying.*—A very important part of emulsion making is now to be touched upon, viz., getting rid of the water held in the pellicular mass.

To commence with, as much water as possible should be squeezed out, and then we may proceed in one of these ways.

1st. We may lay it out flat on a piece of blotting-paper, and allow it to dry spontaneously. 2nd. We may put it in a flat porcelain dish, and place it in a water bath, the temperature of which can never exceed  $212^{\circ}$ , and thus all moisture may be got rid of. In this proceeding the very greatest care is necessary, as the emulsion is



apt to become very hard indeed—so much so as to be scarcely soluble ; in addition to which, it is often apt to blacken spontaneously. The third method is one which we can confidently recommend for washed emulsion, being very simple, and absolutely improving its qualities when re-dissolved. This is simply to cover it with rectified spirit .820 after as much water as possible has been squeezed out. In an hour's time the excess is drained off, and the pellicle is squeezed in the cotton rag as before. It is then once more covered with the spirit, and left for half an hour, when, after draining away the superfluous spirit, it is ready for re-emulsifying. If it be desired to keep the pellicle in a solid state, it will only be necessary to expose it to the air for a few hours, when it will be found quite dry.

It is instructive to examine the washings from the spirit. It will be found that there is a certain small quantity of silver bromide in suspension, which can be filtered out. If the spirit be distilled over, a semi-opaque liquid residue will be left, having a very high boiling point, a strong and very disagreeable smell, and containing some organic salt of silver, which discolours in the light. It may be said that this organic compound is necessary for density of image ; but a trial of the emulsion washed in this way will prove the contrary ; in addition to which, it will be found much freer from spots than that washed and dried by the first two methods indicated above.

There are some pyroxylines which it would be dangerous to treat in this manner, since they are soluble, to a certain extent, in absolute alcohol ; but it seems to the writer that any such pyroxylines are detrimental when washed collodio-bromide emulsion is in question. If they are employed, the old method of drying must be adopted.

The dried (or moist with alcohol) pellicle has next to be dissolved in its proper proportions of solvents, which are about 5 grains of pyroxyline to every ounce of the two when mixed. It is better to make it up first to the strength

of 10 grains of pyroxyline, and then to add the remaining solvents, since the colour of the emulsion seems to be better when a greater degree of viscosity is present when the pellicle begins dissolving. In two or three hours the whole of the silver bromide should be in suspension. It will be found, however, that there is an improvement in the quality of the film after the lapse of a couple of days, or even more. A plate should be tried, before diluting down the collodion with more ether and alcohol, in order to test its flowing qualities, and to note the opacity of the film.

In our own experience we like to be able to see the light from a gas jet through a film whilst moist, but which, when dried, is perfectly opaque. In this condition the film is tough, requires no backing, and is always capable of giving sufficient density by alkaline development alone, without resort to intensification.

Before taking into use, it should be filtered through cotton-wool (see Chap. XVI.)

The exposure necessary for the washed emulsion already described is very constant; with a lens of aperture  $\frac{f}{20}$ , and in a fair light, thirty seconds will be found to be ample when using the alkaline or ferrous oxalate developer.

## CHAPTER VIII.

### CAREY LEA'S CHLORO-BROMIDE EMULSION.

IN the year 1869, Mr. Carey Lea, the able American photographer and experimentalist, brought forward what is known as the chloro-bromide process, in which the new feature of the introduction of a chloride into a bromide is announced, by *preference using cupric chloride*.

The excess of silver employed by Mr. Lea in this process was very little over that required for the full saturation of the bromide and chloride, and after keeping beyond a certain time, in the writer's experience fog was always present when this formula was followed. Mr. Lea himself seems to have found this, for in March of 1870 he introduced a modification of this process, which enabled any amount of excess of silver nitrate to be used, without any danger of fog being produced in development. By this modification the theoretical considerations, subsequently worked out by the writer, and already pointed out, were fulfilled.

The following is the mode of preparation of Mr. Lea's emulsion given in Mr. Lea's words:—

#### *Collodion.*

Ether	...	...	...	20 fluid ounces
Alcohol	...	...	...	12     "
Pyroxyline	...	...	...	162 grains
Bromide of cadmium	...	...	320	"
"      ammonium	...	...	64	"

Add half the alcohol to all the ether, and shake up

with the pyroxyline; throw the salts into a flask with the rest of the alcohol, and heat till dissolved; add to the other portion, shake up well, and place in a warm, light place for three weeks; it will be better still in two or three months.

"This collodion will require 16 grains to the ounce of nitrate of silver to sensitize it. I prefer, and always use, fused nitrate, and recommend it for all collodio-bromide work, as much preferable to the crystallized.

"Having measured out the quantity of collodion to be sensitized, weigh out 16 grains of very finely powdered nitrate of silver to each ounce, throw it into a test-tube or flask, and pour over it alcohol of s. g. .820 in the proportion of 1 drachm to each 8 grains of nitrate; boil for a few minutes, and the nitrate will dissolve; pour it now in successive portions into the collodion, shaking up well after each; shake about five minutes after the last portion is added, and every few times thereafter; use twenty-four hours after sensitizing.

"In twenty or twenty-four hours after sensitizing, the mixture will be in condition to use. The difference of a few hours will not be important, but it is best not to exceed twenty-four. If kept too long, there will be a disposition to fog in the shadows, and a want of brilliancy in the whole picture. The high-lights, also, will not have their details well marked. The filtering is best done by putting a piece of soft, clean sponge in the neck of a funnel, and cutting a small circular filter of close-woven linen. The linen used for making these filters should be boiled for an hour with very weak caustic potash or soda, then well washed in hot water (of course without soap), and dried. This plan of filtering will be found excellent for all sorts of photographic collodions. Before filtering, the collodio-bromide mixture should rest quiet for two or three hours after its last shaking."

For the preservative bath recommended by Mr. Lea (see page 87).

## CHAPTER IX.

### CANON BEECHEY'S PROCESS.

WE have now to put on record a process which is at once simple and efficient, and the thanks of the photographic public are due to Canon Beechey for its explicitness in every detail. The following is the *modus operandi*:—

Take cadmium bromide (anhydrous)	400	grains
Alcohol (.805)	...	10 ounces

and allow the mixture to stand. Decant carefully, and add 80 minims of strong hydrochloric acid.

Take of the above solution...	...	$\frac{1}{2}$ ounce
Absolute ether (.720)	...	9 drachms
Pyroxyline (as above)	... 10 to	12 grains

To sensitize this, dissolve 40 grains of silver nitrate in an ounce of alcohol (.820 sp. gr.) The best method of effecting this is to pound up the silver nitrate in an agate mortar, and to take only a quarter of the alcohol, and boil it in a test-tube containing the silver salt. The alcohol will become slightly brown (due, probably, to the formation of a fulminate of silver), and should be decanted off into a bottle containing the collodion. The remaining silver should be dissolved up in a similar manner, the ounce of alcohol being just sufficient to effect solution.

Between each addition of the silver nitrate the collodion should be well shaken. When the final addition is made, the emulsion should be very smooth, and rather thick. When poured upon a strip of glass plate it will appear transparent by transmitted light, but after keeping twenty-four hours (occasionally shaking the bottle containing it in the interval) it ought to be very opaque and creamy.

The plate having been coated with a substratum, or edged (see Chap. XVI.), the collodion, which should have been shaken about half an hour\* before, is poured on it in the ordinary manner, and, when set, immersed in a dish of distilled or rain water. When all greasiness has disappeared, it is flooded with any of the preservatives given in Chap. XVII. Canon Beechey recommends the plate to be immersed in a dish containing beer to which 1 grain per ounce of pyrogallic acid has been added. The drying is conducted in the usual manner. The exposure may be taken to be about twice that which is necessary for a wet plate. Between exposure and development the plate will keep fairly for a week, but after that it seems to lose detail, and appears under-exposed.

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\* Canon Beechey recommends the bottle to be shaken immediately before use, and the emulsion filtered.

## CHAPTER X.

### M. CHARDON'S PROCESS.

IN preparing the collodion for this process, M. Chardon prefers the use of two kinds of pyroxyline, both of which have previously been precipitated from collodion into water (see page 37). The one pyroxyline is prepared in the manner given at page 37; the other, the high temperature cotton, prepared as at page 38. These are mixed in the solvents to form collodion.

A salted collodion is made up as follows:—

Alcohol	...	...	...	...	1 ounce
Ether	...	...	...	...	2 ounces
Double bromide of cadmium and					
ammonium	...	...	...	...	14 grains
Zinc bromide	...	...	...	...	14 „
Precipitated pyroxyline, ordinary				7	„
Precipitated pyroxyline, high					
temperature...	...	...	...	28	„

A stock of this is made, and, when settled, decanted off as required. It must not be filtered, as the evaporation of the solvents is said to cause a change in the sensitiveness of the finished emulsion, though we doubt it.

The collodion is rendered sensitive in small quantities at a time.



The silver nitrate is finely powdered, the quantities being as follows :—

The above salted collodion	...	1 ounce
Silver nitrate	... ..	6·2 grains
Alcohol	... ..	3 ounces

The ordinary means already described are employed for forming the emulsion (see page 48). The emulsion is vigorously shaken in a bottle, and put aside for thirty-six hours to ripen. After this time has elapsed, about an ounce of pure distilled water is placed in a glass beaker, and a drachm of the emulsion poured into it; after agitating the mixture it is filtered clear, which can be effected by passing it once or twice through the filter paper. This waste is tested for silver nitrate. A slight milkiness on the addition of a chloride is all that is allowable. If it shows no signs of free silver nitrate, more of the latter salt dissolved in alcohol is added to the emulsion just to give the necessary milkiness. This emulsion thus formed is next corrected by a collodion in which cobaltic chloride is dissolved, made as follows :—

Alcohol	... ..	1 ounce
Ether	... ..	1½ ounces
Cobaltic chloride	... ..	60 grains
Pyroxline	... ..	12 „

Of this he adds about two drachms to each 10 ounces of emulsion; as before stated in this work (page 10), all causes of fog are thus eliminated.

The novelty of M. Chardon's process is now to be explained. He takes the finished emulsion, and pours it in a fine stream into a large quantity of water. After stirring, the precipitated emulsion is filtered through a cloth, is washed carefully (the method indicated at page 40 will answer), pressed between folds of blotting-paper, and dried in the dark. This gives a flocculent powder of a

clear yellow colour. To prepare the finished emulsion the following is prepared :—

Ether	...	...	...	...	$\frac{1}{2}$ ounce
Alcohol	...	...	...	...	$\frac{1}{2}$ "
Precipitated quinine	...	...	...	...	1 grain

The precipitated quinine can be made from the ordinary sulphate of quinine by dissolving it in sulphuric acid, and then adding ammonia. The precipitate thus formed is employed.

The organic substance is first dissolved in the alcohol, and, after filtering, the ether is added. To this amount of solvents 17 grains of the dried powder is added. After some hours, when all is in solution, the emulsion is filtered through cotton-wool (see Chap. XVI.) M. Chardon states that the quinine gives porosity to the film; but it seems more probable that it acts like some other organic matters—viz., prevents a tendency to fog.

The exposure for plates prepared by this process is stated to be about double that required for a wet plate.

## CHAPTER XI.

### DAWSON'S PROCESS.

THE next process which we shall describe is one in which an "organifier" is added to the emulsion, and leads up to the more complicated form recommended by Mr. Carey Lea. We are indebted to the *British Journal Almanac* for the formulæ, which are as follows:—

#### *Collodion.*

Pyroxyline	...	...	...	8 grains
Cadmium bromide	...	...	...	7 "
Ammonium bromide	...	...	...	2 "
Ether .725	...	...	...	$\frac{1}{2}$ ounce
Alcohol .810	...	...	...	$\frac{1}{2}$ "

In practice we have found no difference in result, if ether of .730 be used, and alcohol of .812.

In our experience we find that the collodion should be allowed to settle some days, and then be decanted off. The pyroxyline employed may be that given at page 21.

To sensitize this, a mixture is made of—

Silver nitrate	...	...	...	13 grains
Acetic acid	...	...	...	2 drops
Glycerine	...	...	...	1 drachm
Alcohol .830	...	...	...	4 drachms

These are dissolved in the usual manner, it being, perhaps, the better plan to leave the glycerine out till the last minute. After emulsification (page 48) it is allowed to stand twenty-four hours, and then 2 drops of hydrochloric acid are added to the above quantities. It is allowed to rest for another twenty-four hours.

The emulsion is poured out into a dish of sufficient capacity, in order for the solvents to evaporate, and in five or six hours it is ready for further treatment. This consists in covering the pellicular mass with water for an hour, and, after pouring off, covering it *for a similar time* with—

Tannin ...	...	...	...	5 grains
Gallic acid	...	...	...	2 „
Acetic acid	...	...	...	2 drachms
Water (distilled)...	...	...	...	1 ounce

The washing is now commenced in a manner similar to that already described at page 37, till all traces of acid are removed, which can be tested by litmus paper. When all the water is wrung out, the emulsion is dried in a hot water bath, or spread out in a warm room on blotting-paper.

The mode of eliminating all traces of water by alcohol is not admissible in this case, as it would dissolve out the tannic and gallic acid which may be left in the pellicle.

To re-dissolve the pellicle, equal quantities of ether and alcohol are used, having the same specific gravity as that given above. Dr. Dawson recommends that it be soaked in the alcohol for twelve hours before adding the ether.

The development of the plates can be carried out by the strong alkaline development.

## CHAPTER XII.

### CAREY LEA'S CHLOR-IODO-BROMIDE PROCESS.

In this process we have silver iodide emulsified with bromide and chloride, and, in some hands, it works well. The following description will show how the emulsion is prepared. The collodion is made thus—

Ether, .730	...	...	...	4 drachms
Alcohol, .805	...	...	...	4       ,,
Pyroxyline	...	...	...	8 grains.

The cotton may be any of those given in Chap. VI. To every ounce of collodion the following are added:—

Dried cadmium bromide	...	9	grains
Ammonium bromide	...	$2\frac{1}{2}$	,,
Ammonium iodide	...	2	,,

Directly before emulsifying, add—

Aqua regia	...	...	2 drops
------------	-----	-----	---------

The emulsion with an excess of silver is formed by adding 25 to 30 grains of silver nitrate; and after an hour's interval, 2 grains of cupric chloride or cobaltic

chloride ; 2 drops of hydrochloric acid may be substituted for either of these, or for the aqua-regia.


The emulsion may at first appear flakey, but after the addition of the chloride it is only necessary to shake well and leave it for twelve hours. On again shaking, the emulsion will be found perfect. It may be used before drying, or after drying. In the former case, any of the preservatives ordinarily used may be employed.

If it has to be dried, it is poured out into a dish and left till it is in a leathery condition on the surface, after which a preservative is poured upon it. Any preservative will answer, but Mr. Lea recommends

Water	...	...	...	...	6 ounces
Acetic acid	...	...	...	...	3 drachms
Solution of gum-arabic with sugar	4				"
Prepared albumen	...	...	...	...	1 ounce
Gallic acid (60 grains to 1 ounce of alcohol)	...	...	...	...	4 drachms
Tannin (60 grains in 1 oz. of water)	2				"

The albumen is prepared by the addition of an equal bulk of water to the white of one egg, and clarifying with 12 drops of acetic acid.

The gum and sugar solution is made by mixing half-a-pound of gum-arabic and two ounces of sugar in 44 ounces of water, and adding  $1\frac{1}{2}$  drachms of carbolic acid.

The pellicular mass is then broken up, and it and the preservative are transferred to a large glass jar and left there twenty minutes. The preservative is then poured off, and the washing takes place as given at page 52. 

Instead of drying the emulsion, it may be poured direct into the preservative, taking care that the latter is more than four times the bulk of the former. The washing in this case takes place by decantation in the usual manner. This last method is stated to give the most soluble pellicle. The pellicle is then dried in the oven or water bath, and

is re-emulsified by taking for each three ounces of the original collodion—

Ether...	...	...	...	...	1 ounce
Alcolol	...	...	...	...	1 „
Plain collodion (4 grains of pyroxy-					
line to the ounce)...	...	...	...	...	2 ounces

Shake well at intervals, and in a week it is ready for use. The plate is coated in the ordinary manner, and dried. The exposure is about equal to that of a wet plate.



## CHAPTER XIII.

### MR. H. COOPER'S COLLODIO-BROMIDE RELIABLE DRY-PLATE PROCESS.

MR. COOPER'S formula is as follows :—

“ Prepare first a stock of plain collodion by dissolving 160 grains of ordinary pyroxyline\* in six ounces absolute alcohol and ten ounces ether. Good methylated alcohol will answer for these first solvents. as also ether s.g. .730, purchasable at 1s. 6d. per lb. Also make an alcoholic solution of zinc bromide, 80 grains to the ounce. Even after filtering, this solution will throw down a deposit upon keeping, and this must be carefully left undisturbed. To make 10 ounces of washed emulsion, take 5 ounces of the above collodion, and add to it one ounce of the zinc bromide solution, and 20 minims of syrupy lactate of ammonia.† Sensitize with 150 grains of silver nitrate, dissolved first in 80 minims of water, and then in 3 ounces strong alcohol. Boil together, and add it to the bromised collodion at once. I attach importance to the

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\* Mr. Cooper recommends the pyroxyline as prepared by Hopkin and Williams, as answering the purpose.

† “ Small experiments made since this paper was first written go to show that a great gain in sensitiveness may be obtained by reducing the proportion of plain collodion. I have tried three ounces, and even two ounces, instead of the five, with the most encouraging results. I am indebted to a leader in the *British Journal* for the suggestion.”

addition of the boiling solution, so as to raise the temperature of the mixture, and when only a small quantity (such as the above) is made, I take the precaution to wrap the bottle in a thick cloth to retain the heat as long as possible. On examining the portions just given, it will be seen that the silver nitrate is decidedly in excess, and that the alcohol is used in larger proportion than usual.

“Lactate of silver has long been a favourite addition of mine to emulsions, and I am more than ever pleased with its action. I must call attention to a curious effect which is produced if the bromised collodion is allowed to stand many minutes after the lactate is added, and before the sensitizing. The collodion becomes quite milky, and throws down a crystalline deposit. It is well to add the lactate immediately before the silver, or even to defer putting it in until after the sensitizing. I cannot pretend to say what chemical or physical effect occurs in the ‘lactised’ collodion: I merely mention the fact.

“The emulsion is ripe in about twenty-four hours; but I am disposed to think it an improvement to keep it for a longer time, up to three days. At the expiration of the ripening period, twenty minims of strongest nitric acid are to be added, and the emulsion well shaken. I prefer to add the acid just before the washing instead of at first. I believe a better film is given by so doing.

“We are now faced with the question of how best to wash the emulsion. Shall we pour it out and evaporate the solvents, or precipitate it? From a lengthened experience of both methods, I cannot recommend precipitation, except in cases where the finished emulsion is to be used up within a month. It is now a generally acknowledged fact that precipitated emulsions will not keep well. But where large batches of plates can be prepared at a time, and no waste occurs, I can speak to the good qualities of the emulsion when precipitated by mixing it with twice its bulk of the following organifier, and when the pellicle has fully separated and set,

washing for some time in water containing a little nitric acid (half-ounce to one gallon), and finally in several changes of pure water. The mixture—

Tannin ...	...	...	500 grains
Gallic acid ...	...	...	200 „
Grape sugar ...	...	...	200 „
Strong acetic acid	...	...	10 ounces

or a proportionately lesser quantity of glacial, to be dissolved in water, and make up to 100 ounces. This method is expeditious. The alternative, and I think the better plan, is to pour out the emulsion into a sufficiently large dish (1 ounce to 25 square inches, or say 5 ounces in a 12 by 10 dish). Evaporate the solvents more thoroughly than usual; in fact, the pellicle may be allowed to get almost dry. Wash first in water containing half-an-ounce of nitric acid in one gallon of water, and then in plain clean water for some considerable time. If the water in use is hard, distilled water should be used at first and lastly. Wash thoroughly. The extra drying of the pellicle and the large proportion of alcohol it contained will materially assist in shortening the time. When dry, dissolve the above quantity of pellicle in 5 ounces of pure absolute alcohol, and a like quantity of extra purified methylated ether, s.g. .720. An emulsion prepared in this manner with the lactate of ammonia will give excellent negatives without further preparation if the plates are used at once; but its subsequent treatment with alkaline albumen gives the especial qualities for which I had so greatly valued it. The plates are much quickened by the after treatment. This particular emulsion has its sensitiveness doubled, whilst some others are rendered slower.”

Mr. Cooper then describes gelatinizing the plates with gelatine and chrome alum as given at page 77. He says that small plates may have an edging only (page 75), but that he prefers giving them the full coating:—

“Coat with the emulsion. When well set, immerse in water. I myself use a grooved box, well coated with shellac, and when I have coated and immersed as many plates as I intend to prepare, I cover up the box and thoroughly ventilate the room, so as to get rid of all fumes of alcohol and ether before proceeding further. I see no reason why a tin box with removable grooved pieces, similar to the one sent out by the Autotype Company for developing chromotypes, should not answer. Of course it must be kept for the purpose alone.

“The plates are now to be flooded with the alkaline albumen, or dipped in a bath of it. In either case the albumen must be in contact with the film for at least a minute. The plate is then to be thoroughly washed, flowed with a preservative, drained, and dried. After backing it is ready for the camera. The albumen may be prepared in bulk, either with whites of eggs, or with the pure dried preparation. Of the latter, dissolve 60 grs. in 3 ounces of water, and add 1 drachm of strongest liquor ammonia 880. If white of egg be used, first pour in a few minims of dilute acetic acid, and well stir. In two or three hours strain, and to each ounce add two of water and one drachm of liquor ammonia.

“For the ‘preservative’ I have tried a host of substances, and find the simplest of all to be the best—viz., a two-grain solution of gallic acid. For the sake of constant uniformity and certainty, I was anxious to discard from my formulæ all compounds of uncertain chemical constitution, such as beer, or even tea and coffee, or else I could, from my own experience, speak strongly in favour of a decoction of tea, made by boiling 1 ounce of compressed black tea in 4 ounces alcohol and 12 ounces water. One ounce of this is diluted with 10 ounces of water to form the final coating for the plate. It is of importance that the plates should be thoroughly dried, especially if intended for packing; as although these plates will stand exposure to a moist atmosphere better than

most others, any damp remaining in the films when they are stored away will be a source of future trouble."

Mr. Cooper recommends a full exposure in the camera for these plates. We have found that with a stop  $\frac{f}{20}$ , and in an open landscape and good light, thirty seconds are ample; but that three minutes may be given without detriment. Of the negatives produced by this process, Mr. Cooper says:—

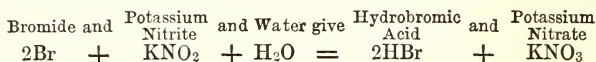
"First, the quality of image is almost perfect, much resembling that given by a really good collodio-albumen plate. Secondly, the films will keep for a lengthy period without deterioration, both before and after exposure. I exhibit a negative which was kept five months before exposure, remaining for three months in a dark slide, and carried about on long journeys, being submitted to many variations of temperature and hygroscopic conditions of the atmosphere. After exposure and before development it was kept five weeks. Other plates have been kept three months after exposure. I give these data, as many folks' ideas of a 'lengthy period' are various. I have plates prepared early this year which I am keeping on to test from time to time.

"In exposure, very great latitude is allowable—an unspeakable boon to the photographer on a tour, with no inconveniences for developing a trial plate from time to time."

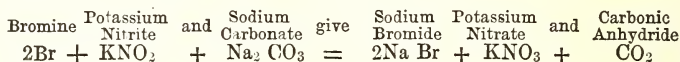
## CHAPTER XIV.

### COLLODIO-BROMIDE EMULSION WITH EXCESS OF BROMIDE.

THE writer, in some recent investigations, was led to the conclusion that, theroretically, the loss of sensitiveness due to using a collodio-bromide emulsion with an excess of soluble bromide must be due to the want of a bromine absorbent; and that if, with an excess of soluble bromide, we had the presence of such an absorbent, that then the sensitiveness should be in a great measure restored. When light causes the liberation of bromine from the silver bromide (see page 9), and when a bromine absorbent, such as potassium nitrite, is present, we have the following reaction:—



The hydrobromic acid liberated would have a tendency to destroy the image; hence it is desirable that a neutral compound should be formed. This will be the case if an alkaline carbonate be added, for then we have—



This practically was proved to be the case. In making a washed emulsion with excess of bromide, it will be



well, then, to add to every ten ounces of emulsion two drachms of a saturated solution of potassium nitrite in alcohol, and to apply to the film sodium carbonate in the first wash water, and then to wash again. By this means the retarding effect of any trace of soluble bromide left is counteracted by the presence of the trace of potassium nitrite and of sodium carbonate.

The following formulæ will be found to form a very excellent emulsion, giving very beautiful films, which, for sensitiveness, are not behind those which are prepared with excess of silver nitrate. It is based on the alteration which is caused in the molecular structure of silver bromide by the use of ammonia, as adopted for the gelatine process.

The ordinary collodion is formed as follows :—

Pyroxyline (high temperature)	25	grains
Alcohol ... ..	2	ounces
Ether ... ..	2	„

To this is added 100 grains of zinc bromide.

In order to emulsify this, 100 grains of silver nitrate are dissolved in the smallest possible quantity of water, made up to 1 ounce with alcohol, s.g. about .820, and liquor ammonia added, drop by drop, till the oxide first precipitated is re-dissolved. The emulsion is then formed as given at page 49. It is immediately placed in a dish to evaporate (see page 50), when it is at once washed till it shows no alkaline, or a very faint trace of alkaline, reaction. The water may be eliminated by the alcohol plan, or by drying, as given at page 52.

The pellicle is then dissolved in  $2\frac{1}{2}$  ounces of alcohol and  $2\frac{1}{2}$  ounces of ether. It will be noticed that the proportion of pyroxyline to silver bromide is too small. Plain collodion made as follows should therefore be judiciously added, till a silver of good quality is obtained :—

Pyroxyline ordinary	...	...	50	grains
Ether .720	...	...	5	ounces
Alcohol .805	...	...	5	„

This must be added judiciously. It will probably be found that as much as 5 ounces of this will have to be added; but a good deal depends on the quality of the pyroxyline.

The emulsion should be orange when mixed, and also after washing. It should be powdery to the touch when a plate is coated with it. It will be found to be as rapid as a wet plate, and if a preservative be used (see Chap. XVII.) which will stand the employment of undiluted ferrous oxalate, it will be found, if rightly prepared, a good deal more sensitive. The development takes place by the alkaline method if preferred. An emulsion may be made by the same formula as above, omitting the ammonia. It will be found slower.

## CHAPTER XV.

### COLLODIO-ALBUMEN EMULSION.

THE writer introduced to the photographic public an emulsion made with albumen, which proved to be very sensitive, and some skilled photographers were pleased with it. The process is given here, as it may, perhaps, be used as a starting point from which other emulsions may be satisfactorily deduced. In the hands of the writer the images were inclined to be thin, but when chloride is introduced it is found that this lack of density vanishes to a great extent, and leaves a very delicate and printable image. The following is the mode of preparation:—16 grains of ordinary cotton are dissolved in 6 drachms of ether ( $\cdot 730$ ) and 4 of alcohol ( $\cdot 805$ ), and the plain collodion thus formed decanted. 20 grains of zinc bromide are dissolved in a small quantity of alcohol, and enough bromine water added to tinge the solution with a very pale yellow. This is added to the above amount of plain collodion. For each half ounce of the above, 1 grain of dried albumen is taken and dissolved in the least possible quantity of water, or 8 drops of the white of an egg may be dropped into a drachm of alcohol, and thoroughly stirred. Either of these solutions is then carefully dropped into the collodion (placed as usual in a jar), and well stirred up. This should form an emulsion of albumen in the collodion. Forty grains of silver nitrate are next added in the way pointed out on page 33, after having

been dissolved in the smallest possible quantity of water and boiling alcohol. A beautifully smooth emulsion should result from this. Mr. Berkeley, who has tried this emulsion, proceeds in a slightly different way: he adds the cotton to the ether, then adds the albumen, and finally adds the amount of zinc bromide in the necessary amount of alcohol.

The amount of silver nitrate added ensures that there is an excess of at least two grains in each ounce of the emulsion

Instead of the emulsion being made entirely with zinc bromide, greater density may be obtained by omitting four grains of it, and adding four grains of calcium chloride.

The emulsion is next poured out into a dish, and the ordinary manipulation carried out. After a couple of washings it may, however, advantageously be covered with a weak solution of silver nitrate, and again washed till the traces of silver are very faint.

The pellicle should be re-dissolved in equal quantities of ether and alcohol, and finally there should be about seven grains of the pyroxyline, as originally used, to each ounce of the mixed solvents.

The emulsion, when finished, generally gives a tender blue by transmitted light, and is seemingly transparent. It may have a tendency to curl off the plate on drying, in which case the addition of a little ordinary washed emulsion will correct it. It will develop with plain pyrogallic acid, and can be intensified by pyrogallic and citric acid, with the addition of a few drops of silver nitrate solution, or it can be developed by the alkaline developer, or the ferrous oxalate developer (page 51), or the hydro-sulphite developer (page 54). Some photographers have found a tendency in it to form blisters when developing. This has not happened to the writer when the developer was kept above 60° F. In some hands this emulsion is extremely rapid—so much so, as to require very considerably less exposure than an ordinary wet plate.

## CHAPTER XVI.

### PREPARATION OF THE PLATE

WHEN we require a glass plate to use without a substratum, we usually soak the plates in nitric acid and water, and then wash under the tap, and carefully dry with a cloth; a cream of tripoli powder in alcohol is then rubbed over the plate, and allowed to dry. When a plate is required for use, the tripoli is rubbed off with a soft cloth, and it is left unpolished; a small piece of blotting-paper is then folded up in the shape of a small spill, and dipped in a solution of albumen in water (the strength is immaterial), and the plate is given an edging by placing the moistened end of the spill beneath the thumb of the right hand, and drawing it round the edge of the plate. By this means a "safe edge" is given to it. The amount of fluid required is so small that the first edge may be dry before the last is finished, and yet sufficient for the purpose will be on the plate.

Some persons rub French chalk or talc over the surface of the plate, and this will be found effective when using washed emulsion, without giving an edging; but we honestly confess that where a preservative is used, this is hardly sufficient. In our own experience a film will adhere to the surface when it is only *once* wetted with water, but not twice. In this case a substratum must be

employed to cause the necessary adhesion of the film to the plate. The following answers :—

Sheet gelatine	...	...	75	grains
Distilled water	...	...	60	ounces
Ammonia	...	...	$\frac{1}{4}$	ounce
Alcohol	...	...	1	„

The gelatine should be first softened in half the quantity of water, and the remainder added in the boiling state, which will dissolve it; when cool the ammonia and alcohol should be added, and it should be carefully filtered.

The late Mr. Henry Cooper introduced a new gelatine substratum, the preparation and application of which he describes as follows :—

“ Soak 60 grains of Nelson’s photographic gelatine in water, drain, and pour on enough boiling water to make 8 fluid ounces. Now add 2 drachms of a ten-grain solution of chrome alum, and stir vigorously for a minute or two. Filter the solution through paper into a clean measure, keeping it warm and avoiding air-bubbles.

“ To save trouble, a large quantity of each of the solutions, the gelatine and the chrome alum, may be prepared, and will keep for a long time if a little pure carbolic acid be added to each. No more must be *mixed* than is required for the batch of plates, as when the compound solution has once become cold, it cannot be again liquefied with heat. The measure and filter used must be well washed with warm water as soon as done with, for the same reason.”

Albumen may also be used.

White of egg	...	...	...	1 ounce
Water	...	...	...	100 ounces
Ammonia	...	...	...	5 drops

50 grains of dried albumen may be substituted for the white of egg. The albumen and water should be well shaken together in a bottle for five minutes, and then be filtered through fine filter-paper, taking care to avoid air-bubbles.



A better formula, however, seems to be one due to Mr. Ackland, and is thus described by Mr. W. Brooks :—

The whites of fresh eggs are collected, and to every 8 ounces, one ounce of water and 24 drops of glacial acetic acid are added, by pouring it into the albumen in a fine stream, and stirring evenly with a glass rod for one or two minutes. The albumen should on no account be beaten or whisked up, or the resulting preparation will be milky. It is allowed to rest one hour or more, and is then strained through coarse muslin or cheese cloth. To the strained albumen is added one drachm of the strongest liquid ammonia ( $\cdot 880$ ), when it can be put away in corked bottles and kept for use.

To make a substratum Mr. Brooks takes—

Prepared stock albumen	...	1 ounce
Water	... ..	1 pint

This is applied as above.

The latest substratum, and which is due to Dr. Vogel, is as follows :—Place (say) 50 grains of gelatine in a flask, and add to them about 2 ounces of acetic acid (it is not necessary for it to be glacial); warm in boiling water to dissolve the gelatine. This amount of acetic acid may not be enough; if so, add more. It is not very particular how much you add, so long as it is sufficient. When dissolved, make up to about 5 ounces with ordinary methylated spirit. At first the solution remains opalescent while the alcohol is added, but at a well-marked point it becomes white, due to the precipitation of the gelatine. No more spirit must be added at this stage, but more acetic acid must be dropped in till the white curdy appearance is lost. The liquid should be heated to aid the re-resolution. A grain of chrome alum dissolved in 1 dr. of water must next be added. You then have a fluid which, when poured upon a glass plate, gives a most excellent substratum. To use it, filter through paper, and coat the plate as with collodion;

return the excess into the filter, rock the plate to do away with many lines, and dry over a Bunsen burner, or a spirit lamp, or before a fire. The alcohol will rapidly evaporate, and then the acetic acid is driven off, and a glassy, hard substratum remains on the surface of the plate. Dr. Vogel directed the plates to be dried spontaneously; but if so, half the valuable qualities of the substratum will be lost. The rapid drying prevents any spots due to dust falling on the plate whilst moist.

The cleaning of the plate is of much greater importance when a substratum is used, than where it is omitted, the great difficulty being to get an even film on the surface. It is impossible to get this if there be the least repellent action between it and water. What the writer recommends is, that the plates be soaked in nitric acid, and be well rubbed with it by means of a pad of cotton wool (*freed from all resinous matter by previous soaking in a strong alkaline carbonate, and then thoroughly washed and dried*), and when the acid is washed away under the tap, that it be followed by a solution of potash 20 grains, alcohol  $\frac{1}{2}$  ounce, and water  $\frac{1}{2}$  ounce, also rubbed in with a pad of wool. When water flows evenly over the surface, the plate should be rinsed in distilled water, and, after a short draining, the gelatine (except Dr. Vogel's, see above) or albumen solution should be flowed over it, and drained off immediately. A very thin substratum will thus be given, which will dry rapidly, and be adherent to every part of the surface. Another plan is to use the Blanchard brush. A brush is made of swan's-down calico, as follows:—A strip of glass, about six inches long by two broad, should be procured, and round one end should be attached, by thread or india-rubber band, a double fold of swan's-down calico. This brush should be dipped in the albumen, and the excess squeezed out against the beaker. The plate, which should be dry, should then be brushed smoothly down the surface in parallel lines to within one-eighth of an inch of its edges,

set up to dry on blotting-paper, and protected from dust. When dried (which should be done spontaneously), the plate will be ready for the collodion.

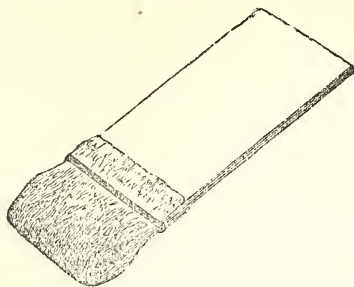


Fig 10.

Some photographers recommend the use of india-rubber for the substratum.

India-rubber	...	...	...	1 grain
Chloroform	...	...	...	1 ounce

Or,

India-rubber	...	...	...	1 grain
Benzoïe	...	...	...	1 ounce

These are flowed over the plate like collodion, the plate, of course, being dry. Unless the solutions be very clear, and free from all residue, a negative taken on a plate so coated is apt to show markings. There are, however, some emulsions which seem to be totally independent of the character of a substratum, and will not show these markings, even when the india-rubber solution is not bright.

*Coating the Plate.*—When plates are to be coated, the emulsion should be well shaken for three or four minutes, and be then allowed to subside for ten minutes. The top portion should then be filtered through cotton-wool, boiled in soda, and then thoroughly washed. The cotton-wool should be placed in the neck of a funnel, and

not be too tightly pressed down; and a little strong alcohol passed through it to moisten it. The first lot of emulsion passing through the funnel should be returned to the bottle, and filtered again. The amount of emulsion required varies with the number and size of the plates used. A trial plate is first coated to see if the emulsion flows readily. If it appears to "drag" over the surface, it should be diluted with a little ether and alcohol (2 parts of the former to 1 of the latter). It will be found that in coating a large plate the emulsion should be thinner than for a small plate. When it appears satisfactory, the emulsion should once more be passed through the filter. Coating the plates is next taken in hand. The filtered emulsion is poured over the plate in the usual manner, and the plate tilted up, and rocked to and fro till the ridges and furrows, so often visible in these plates, have disappeared. The surplus collodion should be returned through the filter into another bottle, as by so doing a fresh portion of the emulsion is used for each plate coated, and there will be a consequent freedom from specks due to any dust which may have fallen on a plate previously coated. If this be a washed emulsion, it should now be dried or treated with a preservative (see Chap. XVII.) If it is to be dried, there is nothing so convenient as a hot air bath, such as used by chemists in their laboratory. They can be obtained up to a size which will take  $8\frac{1}{2}$  by  $6\frac{1}{2}$  plates. It is a good precaution to line the inside with varnished paper, to prevent the remote chance of any metallic specks depositing on the plate during drying. If this be not at hand, the small piece of apparatus recommended by Woodbury is very effective. It consists of an iron tripod stand, such as used in the laboratories, a flat sheet of cast iron,\* and a spirit lamp when gas is not available. The iron plate is placed on the iron tripod, and the spirit lamp beneath it. It is advisable to

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\* An old pikelet iron, in one instance we are aware of, has been successfully employed.

place a couple of pieces of blotting-paper beneath the plate which is to be dried. By using the blotting-paper the plate will be dried and heated uniformly throughout, which is not the case when it is placed directly on the cast iron plate, for curvature in either will prevent the two surfaces coming in contact. The heat should be so great that to touch the surface of the blotting-paper is unpleasant to the fingers, and the glass should be allowed to assume the same temperature. It may be laid down as a maxim that the more rapid the drying, the greater freedom there will be from all spots.

Where a preservative is to be employed with a *washed emulsion*, the plate must be washed with water till all greasiness disappears, when it may be applied at once. If an *unwashed* emulsion be used, the plate must be well washed in distilled water, till all excess of haloid salt, if that be in excess—or, *as a rule*, of the silver nitrate, if that be in excess—be thoroughly eliminated. The preservative may then be applied by flooding the film with it, or by immersing the plate in a flat dish or dipping bath containing it. The plates are in this case usually allowed to dry spontaneously, but they are generally improved by a final dry over the iron plate as directed above.

In Chapter XVII. will be found a description of preservatives which may be applied to washed emulsion with success.

As the result of very numerous experiments, the writer has unwillingly come to the conclusion that a washed emulsion without a preservative of some kind is a dangerous process in which to place absolute trust. Films which would give perfect negatives, free from those spots which refuse to develop, may, after keeping some time, show them in perfection, spoiling every picture taken upon them. An interesting experiment is to take a plate freshly prepared, and expose half of it to sunlight to darken it, and, after the lapse of a fortnight, to expose the other half. Though the first part may show a perfectly uniform



darkening of the surface, the other half will, in all probability, show the spots by their refusal to darken in certain places. A plate used with a preservative, on the other hand, will blacken equally after any length of keeping. The cause of these spots is rather obscure, but we think we have traced them to a quite unsuspected cause, which, if it prove correct, will indicate another use of the preservative. It must be remembered that the ordinary washed emulsion will be free from the objection if the plates are prepared one day, and exposed and developed within three or four days. This lapse of time is often sufficient for the amateur.

*Backing the Plate.*—With some kinds of emulsion, more particularly if a gum or albumen preservative be used, the films are very translucent, and the image is subject to the well-known blurring due to light scattered by the silver compound, and reflected from the back of the plate. This defect is in a measure cured by applying some non-actinic varnish to the back of the plate. This backing may be made as follows:—

Powdered burnt sienna	...	...	1 ounce
Gum	...	...	1 „
Glycerine...	...	...	2 drachms
Water	...	...	10 ounces

The solution can be brushed on with a hog's bristle brush. Ordinary printers' paper coated with gum-arabic, stained with aurine or a blue absorbent dye, and fastened on the plate, is as clean a method of backing a plate as can be desired. Whichever backing is employed, it should be removed previous to the development of the plate, and it is often convenient to do so after the alcohol has been applied to the surface of the film, and before washing with water. The alcohol repels any water containing the soluble part of the backing, and thus prevents staining of the image. A small tuft of cotton-wool will remove the backing given above.



## CHAPTER XVII.

### PRESERVATIVES USED WITH EMULSIONS.

ANY emulsion, washed or unwashed, may be used with a preservative, which ensures the plates being uniformly sensitive, and also the absence of those troublesome spots which refuse to develop. Colonel Wortley says that the thorough washing of the film prevents the formation of these spots; and Mr. Woodbury never finds them when he dries his plates rapidly and at a fairly high temperature. The emulsion used by Woodbury, however, contained resin, and it may be due to this cause that he found the absence of these enemies to emulsion work.

*Beer Preservative.*—The simplest preservative with which we are acquainted is—

Beer	...	...	...	...	1 ounce
Pyrogallic acid	...	...	...	...	1 grain

After the plate is coated, it is washed till all greasiness disappears, and the above is flowed on the film, and allowed to remain on it for a minute. The beer solution may then be drained off, and the plate again washed, or the final washing may be omitted, and the plate be allowed to dry spontaneously. If the plate be washed, it should be given a final rinse of distilled water.

Mr. England recommends, *after* the plate with the beer preservative has been dried, that it should be washed and given a final flooding with a pyrogallic acid solution, one or two grains to the ounce of water. This procedure, he says, immensely increases the rapidity: it is rather more trouble than the methods already given.

If the beer be left on the plate, and if the dimensions of the latter be more than five by seven, a substratum (Chap. XVI.) should be used, as the films may have a tendency to blister. It will be found, however, if, *after exposure*, the plate be washed and be allowed to dry, and then be treated with alcohol and water (page 92), and be developed, that the film will adhere tenaciously to the plate, and that no substratum will be requisite.

Mr. William Brooks, in the PHOTOGRAPHIC NEWS, has recently described a modified method of applying the beer preservative to washed emulsion plates.

The plate is coated in the usual manner, and when properly set it is, *without washing*, plunged into a bath made as follows:—

Bitter ale...	...	...	...	1 ounce
Pyrogallic acid	...	...	...	1 grain

Sufficient of this is used to fill a dish to a depth of half-an-inch. The ale should not be of the kind known as sweet or mild, as both these contain too much saccharine matter. The plate is left in the preservative till there is no repellent action due to the ether and alcohol. It is then taken out and dried spontaneously, a final warming, previous to storing, being given to it by means of a drying oven or a hot water tin. The plates do not require backing unless the emulsion be thin. The exposure necessary must be ascertained by a trial plate.

Mr. Brooks states that he has kept plates prepared by this formula five months before exposure, and about the same time between exposure and development, and has developed them without stain or speck.

The following preservatives may also be used with the emulsion plates.

*Carey Lea's Preservative.*—Mr. Carey Lea's "Litmus Preservative" and tannin preservatives are as follow :—

"Cover a quarter of a pound of good litmus with hot water; set a basin or plate over the bowl, and put in a warm place for a day; throw the paste upon a filter, and pour on hot water till the filtrate amounts to a quart (the filtration is slow); add a drachm of carbolic acid, and the litmus solution keeps good indefinitely.

Litmus solution...	...	...	1 ounce
Water ...	...	...	6 ounces
Gum-arabic ...	...	...	90 grains
Sugar (fine white) ...	...	...	90 "
Acetic acid (No. 8, or Beaufoy's)			25 minims

"The above quantity makes a convenient bath for a  $6\frac{1}{2}$  by  $8\frac{1}{2}$  plate.

"Throw the collodio-bromized plate into a pan of water until the greasy marks are gone, and then pass it into this bath, where it should remain, with occasional agitation, about ten minutes. The time is not important; five minutes will be sufficient; fifteen will do no harm.

The tannin preservative is as follows :—

Water ...	...	...	$7\frac{1}{2}$ ounces
Gum-arabic ...	...	...	90 grains
Sugar ...	...	...	90 "
Tannin ...	...	...	15 "

The washing of the plate is the same as above.

Regarding these two preservatives, Mr. Lea says: the litmus gives the softest and most sensitive plates, but needs an intenser cotton. The latter of the two preservatives will work well with a wider range of pyroxy-lines than the former, and give a brighter picture. The tannin is the easiest to succeed with, but the litmus, when

well managed, undoubtedly gives the best negatives. In either case, the negatives are very beautiful; better looking or better printing negatives cannot be got with the wet process. The development may proceed by the strong alkaline development (page 91), or by the practice as described by Mr. Cooper.

*The Coffee Preservative.*—A coffee preservative is made as follows :—

1.—Best coffee ...	...	...	$\frac{1}{2}$ ounce
White sugar ...	...	...	90 grains
Boiling distilled or rain water			$5\frac{1}{2}$ ounces
2.—Gum-arabic ...	...	...	90 grains
Sugar-candy ...	...	...	20 „
Distilled water ...	...	...	$5\frac{1}{2}$ ounces

When No. 1 is cooled, both solutions are filtered, and the preservative applied by floating or by immersing the washed plate in a flat dish containing the solution.

The plate will require a substratum unless the precaution indicated above be observed.

*Tannin Preservative.*—A simple preservative is made with tannin as under :—

Tannin (pure) ...	...	...	15 grains
Distilled water ...	...	...	1 ounce

The plate is washed, and the preservative applied as above.

*Albumen Beer Preservative.*—The following are prepared :—

1.—Dried albumen (or white of egg, prepared as at p. 79 1 oz.)...	...	...	25 grains
Water ...	...	...	1 ounce
Liquor ammonia ...	...	...	$\frac{1}{2}$ drachm
2.—Ordinary bitter beer ...	...	...	1 ounce
3.—Ordinary bitter beer ...	...	...	1 ounce
Pyrogallic acid...	...	...	1 grain

The plate, after washing, is flowed over with equal parts of 1 and 2, which are allowed to be in contact with the film for one minute. It is then thoroughly washed, and flowed over with No. 3, and set up to dry.

These plates are developed by any of the alkaline developers given in the next chapter. Reducing the amount of pyrogallic acid given to one-third will cause a thin negative, which can be readily intensified by the ordinary intensifier. This preservative gives great beauty and delicacy to the negative, and subsequent intensification is better than getting density by the alkaline developer alone. The plates prepared with the albumen solution are exceedingly rapid and safe.

A substratum is required for large plates.

*Col. Wortley's Preservative* is as follows, and he recommends it as giving freedom from blisters often found with gum preservatives.

The following stock solutions are prepared:—

No. 1.	{	Salicine, enough to make a saturated solution in distilled water.	
No. 2.	{	Tannin ... .. 60 grains	
	{	Distilled water ... .. 1 ounce	
No. 3.	{	Gallic acid ... .. 48 grains	
	{	Alcohol ... .. 1 ounce	

To make the preservative, take of—

No. 1.	...	...	...	2 ounces
No. 2.	...	...	...	1 ounce
No. 3.	...	...	...	$\frac{1}{2}$ "
Sugar	...	...	...	40 grains
Water	...	...	...	7 ounces

This preservative may be used over and over again with occasional filtering. The plates are best immersed in it.

*Red Gum Preservative.*—The following alcoholic preservative may be found useful:—Australian red gum, a

saturated solution, in equal parts of alcohol and water. The plate is washed, flooded with equal parts of alcohol and water, and, after the preservative is floated on, it is dried spontaneously. The gum must be removed by alcohol and water, and the development will take place in the ordinary way. No substratum may be required.

*Gum Guaiacum Preservative.*—This preservative is really mixed with the emulsion itself. It is prepared by making a saturated solution of gum guaiacum in alcohol .805. One part of this to from 20 to 5 parts of the washed emulsion are mixed, and the plate coated in the usual manner. It is allowed to dry at a temperature of about 100°, or else spontaneously. This is an excellent addition to make to a horny collodion.

The writer has tried the above preservatives, and has therefore given them to the reader; but there is no doubt that almost any of the well-known preservatives might have been applied with equal success.



## CHAPTER XVIII.

### DEVELOPMENT OF THE PLATE.

FOR emulsion work, an alkaline (or kindred) developer of some kind is almost an essential, for though faint detail can be developed by pyrogallic acid alone in *most* cases, such a procedure entails a prolonged exposure.

The following are formulæ for the alkaline developer which the writer can recommend, having been in use by him for several years past :

(1).—Pyrogallic acid	...	...	6 grains
Water ...	...	...	1 ounce
(2).—Potassium bromide	...	...	20 grains
Water ...	...	...	1 ounce
(3).—Ammonia	...	...	1 part
Water ...	...	...	32 parts

To develop, 2 parts by measure of (1), 2 parts of (2), and 1 part of (3) are taken and well mixed in the developing cup. If an albumen or gum preservative be used, No. 2 may be reduced to 1 part.

The developer given by Col. Wortley is as follows :—

(a).—Pyrogallic acid	...	...	96 grains
Methylated alcohol	...	...	1 ounce

(b).—Potassium bromide ... .. 120 grains  
 Water distilled ... .. 1 ounce

(c).—Ammonium carbonate ... .. 80 grains  
 Water ... .. 1 ounce

Or,

(c.).—Liquor ammonia .880... .. 6 minims  
 Water ... .. 1 ounce

By the last formula, 6 minims of (a), 3 minims of (b), and 3 drachms of (c) are taken and mixed.

M. Chardon's developer is as follows:—

1.—Ammonium carbonate ... .. 10 grains  
 Potassium bromide ... .. 2 „  
 Water ... .. 1 ounce

(Care must be taken that the carbonate is pure.)

2.—Pyrogallie acid ... .. 50 grains  
 Alcohol ... .. 1 ounce

To develop, the following proportions are taken:—

No. 1 ... .. 1 ounce  
 No. 2 ... .. 10 to 15 minims

The image will appear very rapidly if the emulsion has been properly prepared.

We will now imagine that the plate has been exposed, and that we are to develop the image. After taking the plate out of the slide it is carefully dusted, and, if necessary, a solution of equal parts of alcohol and water is flowed over it to soften the film. It is then either washed under the tap, if the water supply be of good quality, or is immersed in a dish of rain-water previously filtered through charcoal. When all repellent action between the spirit and water is obliterated, the mixed proportions or solutions indicated above are carefully flowed over the plate, and almost immediately poured back. The image ought to appear gradually and without veil. If it shows

unwillingness to appear, a fresh solution should be made, omitting half the bromide, and this will probably be effective.

To develop a plate having a preservative, a little thought should be taken as to the nature of the latter, as has been indicated in the last paragraph. It is evidently useless to waste alcohol if it is not soluble in it. In cases where it is insoluble, the preliminary flooding with the spirit should be omitted, and the soluble matter entirely removed by water. Since the object of the alcohol was to open the pores of the collodion, evidently the same will be accomplished by removing the soluble matter which filled them up.

Should there not be sufficient density, resort must be had to the ordinary acid intensifier.

(1).—Pyrogallic acid	...	...	...	2 grains
Citric acid	...	...	...	2     "
Water	...	...	...	1 ounce

And,

(2).—Silver nitrate	...	...	...	20 grains
Water	...	...	...	1 ounce

The plate must be well washed before using this. Sufficient of No. 1 to cover this plate should be flowed over it, and 4 or 5 drops of No. 2 dropped into the cup, and the solution from off the plate returned on to it. The intensification should then proceed till sufficient density is secured.

The developer which Mr. Brooks recommended for his process is as follows. It is an excellent formula, and as he gives some valuable hints about conducting development, which apply to all processes alike, we give his remarks *in extenso*:—

“After the plate has been exposed, take it on a pneumatic holder, and flow over it equal parts of alcohol and water. I must here add a caution not to use the alcohol

too strong, or it will attack the film unevenly, and cause mottling, especially in the high-lights, as I am sure, from past experience, this is one of the causes. It is not seen so much in the half-tone, and scarcely at all in masses of foliage, or where the subject is well broken up. If mottling does occur, it is most at the thick end of the plate. I do not know if this corresponds with the experience of other workers. If the alcohol is used without diluting (say of a s.g. of .825) the mottled markings are very large, and as the alcohol is diluted with water, they become smaller and smaller till they disappear altogether. I generally allow it to soak well into the film for about two minutes, of the strength mentioned above (half water and half alcohol). Methylated spirit answers every purpose, providing that it is free from gum (if contaminated with gum it turns milky on the addition of water). If a quantity of plates are to be developed, I prefer to immerse each plate in a tray containing the spirit, as it is then done effectually. The plate is then taken and allowed to soak in a dish of clean water, and rocked about until the water flows evenly over its surface. Previous to applying the developer, flood the plate with the following:—

Stock albumen (page 79)	...	1 part
Water	... ..	4 parts

Allow this to soak well into the film; well rock the plate to ensure even action; not less than one minute must be allowed for this part of the operation. The plate is then slightly drained, and the alkaline developer applied, made from the following stock solutions:—

P.—Pyrogallie acid (best)	...	96 grains
Absolute alcohol	...	1 ounce
A.—Sat. sol. ammonium carbonate...		4 ounces
Potassium bromide	...	2 drachms
Water	... ..	8 ounces

A few drops of solution P for 9 by 8 plates (say 5 drops),

and 1 ounce of solution A are mixed in a perfectly clean measure, and at once poured over the plate; as soon as it is covered it must be rocked vigorously for a few seconds, so as to make it blend with the albumen on the plate, and if the plate has been properly exposed the image will at once make its appearance, gradually acquiring intensity.

“After the developer has been on for some little time, should it apparently cease in its action, drain it off, and again apply a little of the prepared albumen solution for about half a minute; drain again, and apply the alkaline developer as before: the image will then, perhaps, rush out very rapidly. This method can be repeated as often as necessary; but, as a rule, with a properly exposed plate, one application of the albumen is sufficient. If more density is required, a drop or two more of P solution can be added. If too much pyrogallic is used, a very hard negative is the result, so it must be used with judgment. I have actually developed a 24 by 18 plate to full printing density with only half a grain of pyrogallic. The formula given for solution A is given for work under normal conditions. In the winter time the bromide can be reduced one-half, and in very warm weather it can be increased.

“I have used the albumen as given above for several years, and the more I use it the more I like it, as it gives an image so much like a good wet plate taken under the best conditions.

“Should it be desirable, the intensity can be brought up in the ordinary way before fixing with acid pyrogallic and silver, same as for wet plates. The plate must be well washed to free it from all traces of ammonia, and before the silver is added to the acid pyrogallic it is first applied to the plate alone, which will generally be sufficient to neutralize whatever may have remained in the pores of the film.”

Some prefer to develop their plates in a dish; indeed, for ease of manipulation, a dish is highly desirable. Care

must be taken in this case that sufficient solution be taken fully to cover the plates; for an  $8\frac{1}{2}$  by  $6\frac{1}{2}$  plate, and an ordinary 10 by 8 porcelain dish, 4 ounces will be required.

The next developer, and that one which seemingly will become a general favourite, is the ferrous oxalate developer, first formally introduced by Mr. W. Willis, Jun., though Mr. Carey Lea pointed out previously that it could be used.

The modes of preparing the ferrous oxalate solution will be found in the Appendix. Our mode of procedure with the developer is as follows:—If the saturated solution of the developer (made by dissolving ferrous oxalate in a saturated solution of potassium oxalate) be used, we dilute it with half its bulk of water, and add to every ounce 1 drachm of a solution of potassium bromide in water (20 grains to 1 ounce), and apply this to the film after washing, as described above. If the image appears slowly, we add half the original quantity of the ferrous oxalate undiluted, and then, if the exposure be anywhere near correct, this will bring up the requisite density. Should more density be required, we intensify as given at page 93.

Should the image refuse to come out even with the stronger developer, one drop of a 10 per cent. solution of sodium to each ounce of hyposulphite developer will have an accelerating effect (see page 19).

The exposure required for this developer seems to be about two-thirds of that required for the alkaline developer given above, and is, therefore, a decided gain to the photographer.

There is a great charm in this developer, the plates gaining intensity steadily, and without any tendency of being overdone, and the negatives give brilliant prints.

A modification of the ferrous oxalate developer, which, for the sake of perspicuity, the writer calls citro-ferrous oxalate, is also applicable for development. It works rather slower, but can be used without the addition of



*any bromide.* The method of preparation will be found in the Appendix. The stronger solution there given is used without potassium bromide, and the development modified and carried on as above described for the ferrous oxalate. The sodium hyposulphite may be used with it as with the ferrous oxalate developer. The ferrous citrate developer as introduced by Dr. Eder is a very feeble developer (see Appendix for formula), whereas the ferrous-citro-oxalate is exceedingly energetic, and is one which the writer can recommend.

There is another developer, originally introduced by M. Sammann, of Paris, which is popularly called the "hydrosulphite developer." It has not been much employed, owing to the trouble there is in making it. It is, however, very effective; and Mr. Berkeley recommends it strongly.

We give M. Sammann's last directions. Make the following stock solutions:—

- |                                      |     |     |     |           |
|--------------------------------------|-----|-----|-----|-----------|
| (1).—Pyrogallie acid                 | ... | ... | ... | 1 ounce   |
| Saturated solution of salicylic acid |     |     |     |           |
| in water                             | ... | ... | ... | 20 ounces |
| (2).—Sodium bisulphite               | ... | ... | ... | 1 ounce   |
| Sodium sulphite                      | ... | ... | ... | 80 grains |
| Water                                | ... | ... | ... | 4 ounces  |

20 grains of sodium borate may be substituted for the sodium sulphite.

When it is required to make the sodium hydrosulphite, a vial is half filled with granulated zinc, and enough of (2) solution is poured in to fill up the interstices. After half-an-hour the reaction is complete. The solution is poured off into a stoppered bottle, where it will keep, but only for a few hours.

The zinc and vial must be well washed, in order to be ready for the next quantity which may be required. M. Sammann says that the bisulphite must be quite free

from sulphurous acid, which, if present, must be neutralized by sodium carbonate. One part of the bisulphite should dissolve in two of water at the ordinary temperature.

Before development, the plates are flooded with a solution of—

Tannin	...	...	...	...	10 grams
Water	...	...	...	...	1 ounce

They are then washed and drained. One part of No. 1 and four parts of No. 2 are then mixed together, and placed in a dish containing the plate, which it is just big enough to hold. When all the detail is well out, it is probable that the negative will have sufficient printing density, as the development is very slow and gradual. If the pyroxyline be of too "organic" a character, a white veil is sometimes seen on the shadows, which, however, disappears on varnishing. Intensity, if it be lacking, may be given in the usual manner by pyrogallie acid and silver, according to the formula given at page 93. Mr. Berkeley states that this developer may be made alkaline with ammonia, in which case the sodium sulphite may be omitted.

The colour of the negatives produced by the above developers varies very much. By the alkaline method we may have a tint of deposit from olive green to brick red; a great deal, seemingly, depends on the fineness of the original silver bromide. The finer it is the redder will be the film, whilst a black deposit is probably coarser than any other. A deposit which is bluish when viewed by transmitted light is probably intermediate between the two, an olive green tint again lying between the reddish and the blue.

The ferrous oxalate and ferrous-citro-oxalate developer gives a blue black deposit, as a rule, and is coarser than that given by the alkaline or hydrosulphite developer. The rapidity of development must also influence the colour, since whatever method be adopted, the metallic

silver is deposited, as well as reduced, more particularly in the alkaline method.

A negative that is fully developed by any of these methods should show reduced silver bromide next to the glass plate in the most opaque parts; so complete should this be, that if the image be dissolved away by nitric acid, we should have a positive picture left behind formed of unaltered bromide, having perfect gradation.

In the early days of emulsion making a weaker developer was made use of, and as for some plates it is still useful, we insert it here for the guidance of students.

No. 1.—Pyrogallic acid	...	...	3 grains
Water...	...	...	1 ounce

(This will not keep long, but should be made when required.)

No. 2.—Ammonium carbonate	...	1½ drachms
Water...	...	1 ounce

Or,

No. 2.—Liquor ammonia	...	1 part
Water...	...	12 parts

No. 3.—Potassium bromide	...	1 grain
Water...	...	1 ounce

No. 4.—Silver nitrate	...	20 grains
Citric acid	...	25 „
Water...	...	1 ounce

Nos. 2, 3, and 4 will keep infinitely.

The film should then be well washed under the tap. If there be every reason to suppose that proper exposure has been given, make a developing mixture in the following proportion :—

No. 1	...	1 drachm
No. 2	...	1 drop
No. 3	...	„

Sufficient should be taken to well cover the plate. Nos. 2 and 3 should be first dropped into the developing cup, and finally No. 1 is added. (The necessity of stirring is prevented by this procedure.) Flood this over the plate. The image, if everything be *en règle*, should appear quickly, and the developer should be worked over the plate till all detail appears by reflected light. When this happens, another drop of No. 2 to each drachm should be dropped into the measure, and the solution poured back onto it as before, and the intensification with the stronger ammoniacal solution proceeded with. The intensity will gradually be increased, and it may happen that the requisite density will be obtained. Should the density not be sufficient, one drop of No. 4, with a drachm of No. 1, may be mixed, and intensification takes place in the ordinary manner. In the writer's experience, the colour and printing qualities of all negatives by this process are improved by even a slight application of the intensifier.

Should the negative flash out at once on the application of the first developer, it is a sign of over-exposure of the plate. The developer should immediately be returned to the cup, and the plate washed. Two drops extra of No. 3 must be added to the developer, and the development proceeded with as before. The potassium bromide keeps the shadows bright, and acts as a retarder; so much has it the latter qualification, that if a large quantity be added, the plate will refuse to develop at all. It is better to fix an over-exposed picture immediately the detail is all out, and intensify with pyrogallie acid and silver afterwards.

If traces of the picture refuse to appear in three or four seconds after an application of the primary developer, a fresh developer should be made up similar to the above, *omitting* the bromide of potassium. If the picture refuse to appear satisfactorily when this course is adopted, the plate is hopelessly under-exposed. When the detail is well out, the intensification should be carried on as given at page 93.

*Fixing Solution.*—The negative should be fixed with potassium cyanide or sodium hyposulphite.

Potassium cyanide	...	...	25 grains
Water	...	...	1 ounce

Or,

Sodium hyposulphite	...	...	1 ounce
Water	...	...	6 ounces

The first may be flowed over the plate, but a dipping bath for the latter will be found advantageous for studio work. There are some images which will not stand the cyanide, and in rare instances some will not stand prolonged immersion in the hyposulphite; it may be because the metallic silver is in a very fine state of division. This seems all the more probable since we know that in this state it is attacked by the cyanide. When all the bromide is dissolved from out of the film, the plate should be well washed back and front. It is not amiss to give a dip in a solution of alum, as used for gelatine plates, if hyposulphite has been used, since it effectually decomposes it.

## CHAPTER XIX.

### A MOIST EMULSION PROCESS.

MR. MAWDSLEY, in December, 1876, introduced a moist emulsion process which he states gives very certain results, and, when used with a tent, or its equivalent, is admirable, as it allows the plates to be prepared ready for use at home, and the negatives may be developed in the field with the *minimum amount of solutions*. Washed emulsion may be employed advantageously. After coating the plate it is rinsed with water, and the following solution poured over it:—

Glycerine (Price's)	...	...	1 ounce
Albumen (white of egg)	...	...	1 „
Water	...	...	20 ounces

These proportions are recommended when the plates are to be used shortly after preparation. If they are to be kept (say) a fortnight or three weeks, the following may be used:—

Glycerine (Price's)	...	...	2 ounces
Albumen	...	...	1 ounce
Water	...	...	6 ounces

In both cases fifty grains of dried albumen dissolved in one ounce of water may be employed instead of the white



of egg. The time of exposure by this method is the same as that required by the dried plate.

The development that Mr. Mawdsley recommends is as follows :—

The plate is flushed with—

Saturated solution of ammonium					
carbonate	...	...	...	...	1 part
Water	...	...	...	...	1 „

This is returned to the bottle for future use.

An eight-grain solution of pyrogallic acid is then poured over the plate, with a few drops of a ten-grain solution of potassium bromide to act as a restrainer.

When the details are well out, the plate is flooded with

Water	...	...	...	...	5 ounces
Acetic acid	...	...	...	...	2 drachms

This neutralizes the ammonia and arrests development. The plate is now stowed away in a light-tight box, and kept for intensification, &c., at home. If under-exposed, or properly exposed, the plate is intensified after washing and flooding with acidulated water, and fixed. If over-exposed, it is first fixed, and then intensified.

This process is simple where it is desired to develop pictures on the spot. One 4-ounce bottle, two 8-ounce bottles, and one 2-ounce bottle will contain all the chemicals and wash-water that may be required in the field in order to develop one and a-half dozen plates.

## CHAPTER XX.

### COLLODIO-CHLORIDE EMULSION FOR DEVELOPMENT.

IN the previous processes it will be seen that silver bromide forms the staple sensitive salt, though both iodide and chloride have been introduced into the emulsion, but in small quantities. The use of chloride by itself has, till quite recently, been inadmissible, on account of the difficulty of producing a chemical developer suitable for it. Dr. Eder and Captain Pizzighelli found that for gelatino-chloride plates, ferrous citrate in a weak form gave good development. The developer was very weak, however, in the form they gave (see Appendix), and the writer introduced the ferrous-citro-oxalate form, which has proved suitable for collodio-chloride plates.

There are two formulæ for collodio-chloride emulsions, one with excess of silver, and the other with an excess of chloride. For most purposes the latter is the one we prefer, since it can be made and used in a quarter of an hour when required. What is usually called collodio-chloride is totally unfit for chemical development, and it is misleading to class it under this denomination, since it has a large proportion of citrate in its composition. To make the collodio-chloride we proceed as follows:—

Weigh out the following—

Pyroxyline (any easily soluble sort)	...	10 grains
" " " " "	...	5 "
Calcium chloride	... ..	20 "
Silver nitrate	... ..	50 "

Dissolve the calcium chloride in  $\frac{1}{2}$  ounce of alcohol .805, by warming over a spirit lamp. Place the 5 grains of pyroxyline in a 2-ounce bottle, and pour on it the alcohol containing the calcium. After a couple of minutes add  $\frac{1}{2}$  ounce of ether, when the cotton will dissolve.

Dissolve the 50 grains of silver nitrate in a test-tube in the smallest quantity of water, and add to it 1 ounce of boiling alcohol .805, and mix. Previous to this the 10 grains of pyroxyline should have been placed in a four-ounce bottle, and the alcohol containing the silver should be poured on. Next add 1 ounce of ether, little by little, with continuous shaking. The silver nitrate may very probably partially crystallize out, but that is of very little consequence. Take the two bottles into the dark-room (a room glazed for wet-plate work will answer perfectly), and *pour gradually the calcium chloride collodion into the silver nitrate collodion*—on no account *vice versa*. The resulting emulsion, of course, is silver chloride in an extremely fine state of division. A plate coated with it should show a canary colour by transmitted skylight, and a thickish film should make a gas flame appear ruby-coloured. The emulsion may be washed in the usual way, if required (see page 51); but, when washed, and used simply dried after washing, it is, like other collodion emulsion prepared with an excess of haloid, rather insensitive. Before doing anything with the emulsion, however, a plate should be coated, washed under a tap, and placed in the dark slide. The slide should be taken into white light, and half the front pulled up for a second, and then closed. Ferrous-citro-oxalate developer, as given in the Appendix, should then be applied, and the result noted. A blackening of

the film may ensue. If correct on the application of the developer, the film should not show any reduction of the chloride, except on the exposed half of the plate. Should blackening take place, nitric acid may be added; but that rather rots the film if kept too long in contact with the emulsion, which would be the case if it is to remain unwashed. A simpler plan is to add a soluble chloride which would form a double chloride. Three or four drops of a 20-grain solution of cupric chloride (chloride of copper) should be added to the emulsion, and shaken up, and immediately the fog disappears. Two or three drops of gold tri-chloride, or of cobaltic chloride of a similar strength as the copper chloride, would answer equally as well.

So far as regards the making of the emulsion. The next point is the preparation of the plates. As was said before, it can be washed, but we really see no advantage in so doing. Polished and edged plates [(see page 77)] may be coated, washed, and then simply flooded once over with—

Beer	...	...	...	...	5 ounces
Sugar (white)	...	1	moderate sized lump		
Pyrogallic acid	...	...	...	...	5 grains

These, when dry, will be very sensitive, and put to shame many a collodio-bromide emulsion. Any of the preservatives given in Chap. XVII. may also be used. To develop, rinse, and then simply immerse them in a dish containing the ferrous-citro-oxalate. In a short time the image will begin to appear, and gradually gain strength. The colour of the image is a beautiful ivory black, and admirably suited for collodion transfers. If a warmer tint is required, tone in a dish with—

Uranium nitrate...	...	...	10 grains
Ferricyanide of potassium	...	10	„
Water	...	...	10 ounces

The colour will rapidly warm, and would eventually become a pretty chocolate colour.

It will be noted that an emulsion prepared in this way may be developed by the ferrous-citro-oxalate *without any restrainer*.

They will also develop with :—

Hydrokinone	...	...	...	10 grains
Water	...	...	...	1 ounce

to every ounce of which are added 3 or 4 drops of a saturated solution of carbonate of ammonia.

The emulsion may also be made with an excess of silver nitrate, in which case, in the above formulæ, seventy grains of silver nitrate should be used. Fog may be prevented by adding 2 or 3 drops of strong nitric acid to the calcium chloride collodion, or it may be eliminated by the use of bichromate of potash, or by hydrochloric acid, or by cupric cobaltic, or auric (gold) chlorides, after the excess of silver has been washed away. In fact, the same procedure should be adopted as in the collodio-bromide process (see Chap. VII.) The development of this emulsion is carried on as above.

*Collodio-bromo-chloride Emulsion.*—A very capital emulsion is formed by mixing  $\frac{2}{3}$  part of an unwashed collodio-bromide emulsion with  $\frac{1}{3}$  part of an unwashed collodio-chloride emulsion. The same proportion of washed emulsions may also be mixed with advantage. The development of this emulsion is most advantageous when an unrestrained developer such as the above is used.

## CHAPTER XXI.

### DEFECTS IN COLLODION EMULSION PLATES.

IT is somewhat difficult to name the especial defects found in the emulsion dry plates, but we will endeavour to point out the principal ones.

*Blisters in the film* may be due to a preservative, more particularly if it contain gummy matter. Thus, with the beer, or the gum-gallic, or coffee preservatives these may make their appearance. The remedy has already been given.

*Black spots on development* are usually due to dust being allowed to settle on the film whilst drying; decomposing organic matter in fine particles is also a fruitful source of these annoyances.

*Insensitive patches or spots on development* have not yet been tracked to an origin; but if a preservative be employed, they will rarely be met with. They seem to be due to impurities in the pyroxyline, since with certain preparations they are altogether absent.

*Grape markings in the film* are usually due to the solvents of the emulsion being too aqueous; or they may be due to the emulsion not having been shaken up shortly before being used, or to the bromide being too coarse.

*Thin transparent films* with washed emulsion are usually due to the last two causes.

*The emulsion refusing to flow properly* is due to deficiency



of solvents. This is frequently met with if the same emulsion be used for coating many plates. It should be diluted down with 1 part of alcohol ( $\cdot 812$ ) to 2 of ether ( $\cdot 720$ ).

*When the film tends to peel off the plate*, the pyroxyline is probably of too contractile and horny a nature, in which case the proper treatment is to mix it with an emulsion made with one of a more powdery character, or to mix a little gum guaiacum dissolved in alcohol with it.

*Circular insensitive patches in the centre of the plates* are sometimes met with in hot weather, when a pneumatic plate-holder is used.

*The cause of fog* has been pointed out in the first chapter, and need scarcely be alluded to again. To eliminate it in a washed emulsion, the careful addition of a few drops of a dilute solution of iodine in alcohol will prove effective. With such an emulsion, when used with a preservative, a dip in a 10 per cent. solution of hydrochloric acid in water will eliminate all fog. In an unwashed emulsion the addition of nitric acid will effect a cure.

*Plates which fog* through having been exposed to light may be rendered available for use by washing off any preservative they may have on them, and immersing them in a hock-coloured solution of potassium bichromate, or by water faintly tinged with potassium permanganate, or with a 10 per cent. solution of hydroxyl or hydrochloric acid in water. After washing, a preservative may again be applied.

*Plates which fog under development*, when the emulsion is not in fault, must owe this defect to one of two causes: 1st, to the light of the developing room; or, 2nd, to the developer. The first cause is easily tracked, as a plate may be prepared and developed in almost absolute darkness without receiving any exposure to ordinary light. If, after a short application of the developer, no fog is found, the light used during development is in fault. If the plate fogs, the developer is wrong. In this

case, try making up fresh solutions, and using more soluble bromide as a restrainer. With the ferrous oxalate developer want of bromide is often the cause of fog.

*Drying markings in a film* are sometimes met with. They generally form a sort of ripple marking near one edge. They are usually found when impure water is used for the final washing of a plate, and are absent when a final rinsing with distilled water is given. With plain washed emulsion these markings are never met with unless the temperature of the drying oven is high.

*Thick specks in a plate* are usually due to the dried emulsion from the neck of the bottle mixing with the solution and finding a resting-place in the film.

## CHAPTER XXII.

### INTRODUCTORY REMARKS ON GELATINE EMULSIONS.

A GELATINE EMULSION, as it is somewhat crudely called, is in reality silver bromide, &c., emulsified in a gelatine solution, with which plates are coated. We have already (page 3) stated that there are various modifications of the molecular state of the bromide, and that some can be brought about in a variety of ways. Mr. C. Bennett first showed how extremely sensitive plates would be prepared by keeping the gelatine solution liquid at a temperature of about  $90^{\circ}$  for six or seven days. What he accomplished was in reality to bring about a modification which was very easily acted upon by light. It need scarcely be said that in certain states of the weather this long emulsification was attended with enormous risks of decomposing the gelatine, and when gelatine decomposes, the products are apt to reduce the silver bromide to the metallic state, and hence to cause fog. Besides this, there is the danger, even if fog is not produced, of the gelatine refusing to set. Col. Wortley stated that he got the same rapidity in his plates by raising the temperature of the emulsion for a few hours to  $150^{\circ}$  F., and Mr. Mansfield first recommended the gelatine emulsion to be brought to the boiling point; but then a very short boiling is liable to destroy the setting qualities of the gelatine. Mr. W. B. Bolton, in an article

in the *British Journal of Photography*, first indicated the true method of preparing emulsions by boiling. He emulsified in a small quantity of gelatine, boiled, and then added to the emulsion the proper quantity of gelatine to give it a firm consistency when setting. We may say that the publication of this article opened out a new era in gelatine emulsions. We need not explain the *rationale* of the process further. Dr. Van Monckhoven called attention to the fact that by adding ammonia to the silver bromide a modification was obtained which gave great rapidity, and Dr. Eder carried the principle further, and gave a really workable, though in some states of weather a dangerous, process. The great *desideratum*, according to these authorities, was to obtain a grey emulsion by transmitted light, and green by reflected; but, as will be seen from our remarks on page 3, this state is not what we consider the most sensitive, and certainly we have never obtained plates so rapid by the ammonia process as we have by the boiling process. The addition of the ammonia is, as we have remarked, dangerous sometimes, since its presence is very apt to induce fog, owing to gelatine decomposing more rapidly in its presence. We have endeavoured in the following pages to give an accurate description of the way to carry out all these processes. But we here make a distinct record of our opinion, which is, that for rapidity and certainty the boiling processes are the best and safest.

We have also given processes for precipitating silver bromide in water or glycerine and water, and then adding it to gelatine. The processes are effective, but they are not so easily employed where iodide is used, as the iodide is apt to settle down in large particles.

There is a vast amount of experimental work to be carried out in all the gelatine processes. One simple experiment we would wish our readers to try, and that is to prepare gelatine emulsions with silver iodide alone, bromide alone, and chloride alone, and to mix the three in different proportions, and to note the results. We are

sure that the relative value of the different emulsions will be very soon apparent. It is very easy to try and write or talk down a process, and in some cases we feel that this has been done. The only fair way of settling the value of a process is for the individual to try the experiments himself, and form his own judgment; but if the reader has a process with which he is thoroughly satisfied, we advise him to keep to it, and not waste his time or energy in following out more elaborate, but perhaps less successful, processes.

A pertinent question for everyone to ask himself is, as to whether a very rapid process is always a *desideratum*. For our own part we unhesitatingly say it is not. For transient effects in a landscape for instantaneous views, or for portraiture in dull weather, rapid plates are useful adjuncts, but should be nothing more. We believe that finer pictures, more mellow and truthful, are usually produced by the slower plates, be they collodion or gelatine.

## CHAPTER XXIII.

### ON THE CAUSES OF SENSITIVENESS IN GELATINE EMULSION.

It would have been difficult to have treated of the causes which induce sensitiveness in gelatine emulsion in the same chapter as that which treats of the sensitiveness in collodion emulsion ; we therefore determined to postpone their consideration till now. It may be said that in a gelatine emulsion it is almost necessary that the soluble bromide be in excess over the silver nitrate ; that is, that when all the nitrate is converted into bromide, there should still be soluble bromide left in solution. It must be recollected that gelatine is a most unstable body, and we believe we are correct in saying that from the first time it is heated its decomposition commences. This decomposition at first gives rise to an acid reaction, and eventually to an alkaline one. In the first stage no harm will ensue to silver bromide suspended in it ; but when the latter stage is arrived at, there is a great tendency for the silver salt to be reduced to the metallic state, unless some body be present which hinders it. Such bodies are found in acids and soluble bromide. The addition of acid must be made cautiously, since acids cause gelatine to lose its setting properties, and there is, consequently, a greater safety in using excess of bromide. Again, if there were any excess of silver nitrate, it would combine



with the gelatine, and we should have a product formed not particularly sensitive to light, but acted upon by a developer at once, and have in consequence a production of red fog. We may, therefore, take it that in the production of gelatine emulsion an excess of soluble bromide is essential.

In the first chapter we have already referred to the differences in molecular structure that silver bromide may assume ; and we repeat that the molecular structure is purely due to physical causes, and *not* to different chemical composition ; in other words, bromide, chloride, and iodide of silver have always the same proportions of bromine, chlorine, and iodine to silver present.

When silver bromide is produced with proper precautions as an emulsion, or by the bath, as in the wet collodion process, we have the film transmitting red rays, and absorbing the blue rays ; showing that the work performed in the film is really done by the blue rays. If a gelatine emulsion, however, be boiled, the bromide, unless great care be taken in mixing, becomes a cold grey colour by transmitted light, and yellowish green by reflected light, and this shows that some of the yellow and red rays are absorbed, whilst some of the blue rays are transmitted ; and yet it is found that this silver bromide is more sensitive to the blue rays than the redder form. Can any explanation be given of this ? We think it can. It is not owing to the fact that the silver salt is slightly sensitive to the yellow rays, for this would only increase the sensitiveness by about one-twentieth, as photographing the spectrum shows us. It must be recollected that the apparent colour of the bromide may be produced in two ways—or rather, that it may be due to two causes : it may be due to the colour of the silver bromide itself, which is what we may call its molecular colour, or a variation in colour may be due to the scattering of light by the different sizes of the particles, each particle being probably composed of thousands of molecules. When an

emulsion is boiled, an inspection of the films after different lengths of boiling will convince us that the longer an emulsion is boiled, the larger the size of the particles which are embedded in the gelatine. Hence boiling produces large particles. Now, we have shown (page 17) that metallic silver cannot exist in contact with silver bromide, but that the latter becomes at once amenable to development by its conversion into sub-bromide. Suppose, then, that one molecule of one of these particles is affected by light, the rest of the particle would be reduced and give the appearance of increased sensitiveness, and would practically have that increased sensitiveness, since sensitiveness is only recognized by a visible quantity of metallic silver. Thus, if the particles in one were only one-tenth part of the size they are in another, it is quite within the range of probability that the sensitiveness of the former might be concluded to be only one-tenth of the latter, whereas the light would have done precisely the same work on the two. Let us take an example of two kinds of bromide, both apparently having the same size of particles, the one having been produced originally in the orange state, which the spectro-scope tells us is peculiarly sensitive to the blue rays, and the other in a different molecular state, which the spectro-scope tells us is sensitive to the red, but much less sensitive to the blue than the first sort. It will be found that, after boiling these two emulsions, the same ratio of sensitiveness to the blue end of the spectrum is still maintained, and if two plates prepared by the two emulsions be carefully examined by transmitted light, it will be found that the emulsion which was originally of an orange tint still shows a trace of orange colour mixed up with the grey; in other words, there is a mixture of the scattered light, and of the true molecular colour. In order, then, to have the greatest sensitiveness, the first condition is that the original emulsion before boiling must be orange by transmitted light.

There is another point in regard to the boiling of an

emulsion, which is, that silver bromide is slightly soluble in water, *and much more so* in water containing soluble bromide. Without doubt during boiling some portions of the silver bromide are dissolved and re-precipitated, other portions of the bromide being taken up, and they in their turn deposited, and so on.

Mr. Wilson, in his description of his gelatine process (which won the Paget prize), and which statement we overlooked when we experimented on the subject, says :—

“*The proportions of soluble bromide and silver nitrate are very important. Contrary to usual statements, the larger the excess of silver bromide, the more quickly is the AgBr converted; if there be but little excess, a very long cooking will be required; and if exactly the equivalent quantities could be used, the writer believes that no amount of cooking would give the sensitive condition. Too large an excess, on the contrary, tends to form fog, which is not to be afterwards got rid of by the use of bichromate, but which is more liable to occur with alkaline pyrogallic developer than with ferrous oxalate.*”

Practically we have proved that by increasing the proportion of soluble bromide to silver nitrate a great increase of sensitiveness is brought about. We are rather inclined to think that this is due to the fact that when the excess is slight, the water alone plays the part of the solvent of the silver bromide, and re-precipitates it in not the most sensitive form; whereas, when precipitated from water containing a large excess of bromide, the molecular state is the orange state, the boiling, of course, subsequently coagulating these molecules into particles. It will be noticed that ammonia has the same effect when applied to a cool solution, and this we lay to the same cause. It is very doubtful, theoretically, if an emulsion prepared in a cool state can ever be as uniformly sensitive as one which is prepared by the aid of heat, since the molecular aggregations can scarcely be as homogeneous

as when they are subjected to a certain amount of friction to render them so. In our own experience we have never met with an ammonia prepared emulsion which could be as rapid as one can be prepared by boiling.

It might be supposed that a perfectly neutral state or an alkaline state of the emulsion should be conducive to sensitiveness, and seeing the use made of ammonia, there is, at first sight, much in it. Dr. Vogel, however, has, by the production of an acid emulsion (which he classes as sensitive as ordinary gelatine plates), proved that such is not the case. The production of this emulsion, one solvent of which is acetic acid, and in which silver bromide is not soluble, is most valuable in a theoretical point of view (always supposing that no material loss of sensitiveness is produced by it) being one more proof that the sensitiveness is due wholly to a physical change, and not to a chemical change in the silver bromide.

There is another fact of especial interest, which is, that keeping an emulsion after preparation previous to coating the plate is conducive to sensitiveness. The following table will show the increase given by keeping. The increase is gauged by taking the first day's sensitiveness as unity. The emulsions were washed, and melted, and a small portion taken out of the jelly each day.

	1st day.	2nd day.	3rd day.
1st experiment	1	1·7	2·7
2nd        ,,	1	2·3	3·0
3rd        ,,	1	2·3	3·0
4th        ,,	1	3·0	3·0
5th        ,,	1	2·3	3·0

The growth of sensitiveness is here evident; keeping longer than this appears to give no practical increase. We will try to explain this phenomenon theoretically. The editor of the *British Journal of Photography* explains it on the supposition that ammonia is formed in the gelatine by

keeping it, and that this re-acts on the bromide. From what we have said before, this will be seen not to be our view; the amount of ammonia formed would be very small, and as the water is in the jelly, the solvent action would not come into play. Again, another point is that we have found that if the emulsion be slightly acidified the same result is obtained, which is decidedly against the ammonia theory. Our own belief is that silver bromide, to be in the most sensitive state, must be placed entirely beyond any state of strain.\* It is during boiling that this strained state is probably given to the particles of silver bromide, and by subsequently keeping the emulsion in the state of jelly this strain wears off, in a similar way to that in which glass is annealed by being kept in a semi-plastic state. When the bromide is in dried gelatine it exists in the same state of strain as that in which it finds itself before the plate is dried. When emulsion which has not been kept is spread on a plate, and one part rapidly dried, and the other more slowly, it will be found that the part most rapidly dried is less sensitive than the part more slowly dried. In the one case the strain is taken off, and in the other it is not. In the case of an emulsion kept two or three days, the difference in sensitiveness of the slow and quick drying portions of the plate is not apparent. Another cause of apparent diminution in sensitiveness is the use of too hard a description of gelatine, and also the use of too small a quantity of water with it. The greatest part of the sensitiveness is present, but it cannot be developed. The diminution of sensitiveness is here also probably due to the strain on the bromide. We made some interesting experiments regarding this. We had some plates, the emulsion for which was prepared in a very small quantity of water, and the gelatine was very hard. Half of some plates were

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\* We would invite a comparison of the effect of light on silver chloride in the crystalline state as produced by fusion, and in the powder state; even when prepared with an excess of chloride, the latter will darken, whereas the former remains nearly unchanged.



immersed in water for half an hour, and half of others in a mixture of 1 dr. of glycerine to half a pint of water for the same time. The plates were then dried, and exposed. Those portions of the plate which had been wetted with glycerine and water developed out with proper density; the difference with those wetted with water alone was not so marked; the other portions lacked vigour, and were apparently insensitive. To prove whether the sensitiveness had altered by the wetting, plates were exposed, then half of them wetted, dried again, and then developed. There was nearly the same result as before. It will be seen, then, that to get a proper amount of density and sensitiveness the gelatine in the emulsion before coating the plates should have a liberal supply of water with it. Various other experiments have been made, all tending to prove that if great sensitiveness is required, the gelatine should be as soft as is consistent with safety.

Another point which is conducive to sensitiveness should be attended to. If the solution in which the silver bromide is boiled is very viscous, the modification will not take place with any degree of rapidity; on the other hand, fog is induced by having the gelatine too dilute, since the particles are built up too coarsely. Even with the ammonia process, the same holds good, for if an emulsion be formed in cold solutions, according to Eder's plan, with the minimum amount of gelatine, it will be more sensitive by many degrees than if mixed warm with the full amount of gelatine, and digested afterwards for an hour.



## CHAPTER XXIV.

### SILVER IODIDE AND CHLORIDE IN EMULSIONS.

THERE has been some dispute regarding the advantage of the use of silver iodide in emulsions, and we will endeavour to put the matter before our readers without bias. The introduction of iodide in gelatine emulsions was first generally brought to the knowledge of the photographic world in a paper read before the Photographic Society of Great Britain, from which we quote some remarks we then made.

“What can be more miserable than to go into a ‘gelatine’ man’s developing room, and see how he fumbles about for this thing and that, and then finally develops his plate almost by a *tour de force*? I hope to show you how that can be avoided by a very simple means, and I do so with the more confidence as a portion of my experiments have been confirmed by a no unworthy labourer in the same field, Mr. W. England. The modification is simplicity itself. Bromide of silver is sensitive well into the red of the spectrum, as is well known, whilst bromo-iodide of silver is not.

“A year ago I verbally mentioned to a well-known gelatine plate preparer that a modicum of iodide of silver in the emulsion took off the great sensitiveness to the yellow and red rays; and some six months ago, in a letter I wrote to the Belgian Photographic Society, I described

certain experiments therewith. Since that time, at my leisure, I have worked at the process with very definite ideas of what I required, and having found the means of arriving at my requirements, I offer the results of experiment to the Society. I am in a position to say that an emulsion of silver bromo-iodide can be made just as sensitive as the emulsion silver bromide, as regards the ordinary so-called actinic rays, and can be prepared so as to be perfectly unacted upon by the orange or red rays, which is a step in the right direction, according to my way of thinking. If, instead of dissolving soluble bromide in the gelatine previous to precipitating with the silver nitrate, 1-6th part of the quantity of soluble iodide be added, the rays which affect the resulting washed emulsion are nearly those which affect a wet plate; if 1-12th part be used, the compound is sensitive well into the yellow; and if 1-24th be used, the emulsion is slightly sensitive to orange, and a *very* little into the red. To those who use the spectroscope one may speak more definitely. The first is sensitive to the rays above E, the second to the rays above D, and the last to the rays above B, or thereabouts (see page 3).

"Now about sensitiveness. If such salts be emulsified with (say) 1-6th to 1-4th the amount of gelatine to be finally used, and then be boiled for *equal times*, the resulting emulsions will be equally sensitive\* if kept a couple of days, and in the first case the development can take place in a room in which the ordinary wet process is worked, always supposing that the glass, or covering of the window, really admits only orange light. With the last, two proportions—ruby and orange glass combined—are perfect protections during development, which is more than can be said when silver bromide alone is used. It is only recently that I have been undertaking comparative experiments,

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\* This is important, because at first the pure bromide emulsion without the iodide will have the advantage which it more than loses after keeping.

and every emulsion made is actually tried in the photo-spectroscope, so that there can be no doubt as to what rays the substance experimented upon is sensitive. There is another great advantage in the use of iodide even in smaller proportions, and that is the great clearness of the shadows which is often wanting in a gelatine plate. It happened when I was in the midst of my most recent researches in this matter that I visited Mr. England for the purpose of comparing some plates with his, and I found that he also had been experimenting in the same direction, and had arrived at the same conclusion as myself regarding the sensitiveness of the bromo-iodide emulsion, and also its beautiful clearness."

Col. Wortley and Mr. Dawson have stated that in their hands the plates prepared with iodide do not keep,\* and that they are slower than when prepared without it. There have again been others who hold contrary views, amongst whom we may name Mr. England and Mr. W. B. Bolton. Dr. Eder has expressed himself against the use of iodide and chloride, in the following terms:—

"I do not at all see the use of employing iodide of silver in gelatino-bromide. I find that iodide is always much less sensitive than bromide. Bolton, Davanne, Vogel, Stillman, and others, have shown that iodide of silver with alkaline development is scarcely at all sensitive. So in gelatino-bromide of silver, it diminishes the sensitiveness. If to gelatino-bromide be added a quarter to a half of iodide of silver, the plates in studio work become much less sensitive, and the negatives are feebler than with pure bromide of silver. Even the addition of one-twelfth of iodide diminishes considerably the sensitiveness of an emulsion. An emulsion of iodo-bromide

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\* Mr. Dawson has quite recently told us that this is due to hygroscopic conditions, the failure keeping pace with the amount of iodide. What is the connection between silver iodide and the hygroscopic tendency of the film, it is hard to see theoretically. We have never found it out thus ourselves.

of silver with one-twelfth of iodide boiled for half-an-hour is not much more rapid than an insensitive emulsion of simple bromide of silver unmodified and scarcely boiled. Moreover, those plates develop more slowly. The advantage they possess in giving clearness in the shadows, and of being capable of development in a well-lighted dark room, does not compensate sufficiently, in my opinion, for the loss of sensitiveness. And I hold as an enormous advantage the great sensitiveness of pure bromide of silver to different colours—an advantage which should never be given up. The ideal of a photographic plate would be to have the greatest possible sensitiveness towards the red extremity of the spectrum (red, yellow, and green).<sup>\*</sup> This plate would give the effects of natural light, and the play of light and shade would be rendered in the photograph much as it appears to the human eye. Of all the productions at present known, bromide of silver, pure and modified, most nearly approaches this ideal.

“I consider as even more unfavourable than the addition of iodide of silver, the use of chloro-bromide of silver. We see springing up on all sides recipes for chloro-iodo-bromide emulsions. I would strongly protest against all these absurdities. Chloride of silver is reduced with infinitely more ease and rapidity than bromide. It is also tolerably sensitive to light, and receives equally the latent image during the time of exposure necessary to bromide of silver. The strong developer necessary for bromide is, however, much too forcible for chloride. Chloride of silver blackens completely throughout before the bromide is reduced in the lights. Hence there is always fog in chloro-bromide plates, unless there be added to the developer sufficient bromide of potassium to transform to

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<sup>\*</sup> We may remark, regarding this, that the sensitiveness of silver bromide in the state in which it is found in the gelatine emulsion is vastly different for the red, yellow, and blue rays. If the first be said to have a sensitiveness of 1, the yellow may be said to have about 5, and the blue at least 100. We are at present thus very far from an ideal plate.

bromide of silver all the chloride, and thus cause an irregular reduction.

"First, as to the iodide. We must look on it in two aspects: one in which it alters the physical aspect of the film in which it is used; and the second, in regard to the chemical aspect. Now, where alkaline development is used, the iodide is so much inert salt in the film. Supposing (as we always do suppose, and most rigidly cling to) that the iodide, bromide, and chloride of silver are reduced by light to the form of a sub-salt of silver, it may be well to glance briefly at the action that iodide may have."

Supposing iodine is set free after exposure, what becomes of it? and also the bromine, what becomes of it? Iodides of the alkalies will displace bromine in the bromides of silver, as we are all aware, but iodine will not displace bromine, but, on the contrary, bromine will displace iodine apparently till they are in the proportion of their molecular weight. If, then, we have bromine and iodine liberated by the action of light, the bromine will attack the particles of iodide in its immediate neighbourhood, and we have a double quantity of iodine set free. In other words, we have all iodine liberated instead of bromine. At first sight it might seem that double work was here done, so that there was a loss of energy; but a little consideration will show that this is not the case. The only loss of energy which can be taken into account is the difference of the affinities of gelatine for iodine, and of gelatine for bromine. Iodine has a greater affinity for gelatine than has bromine, so that as regards loss of energy, and consequent sensitiveness in this respect, the mixture of iodide has the advantage. It remains, however, to consider, when we may expect that a mixture of iodide with bromide will act prejudicially. This will be when the number of particles of iodide acted upon by light (and which are undevelopable, and consequently a cause of diminution in sensitiveness) bear such a proportion to the particles of bromide that the increased affinity



of iodine over bromine for gelatine is more than counter-balanced. The exact theoretical figures are very difficult to give, but we should say that if a surface contains 1-10th of iodide to 1 of bromide, the sensitiveness would remain the same as when none was used; whilst with 1-20th there should be a small increase. Now as regards the physical state of the silver: we have shown that the addition of iodide acts as a restrainer to fog, and is, of course, not the least a destroyer of the image. In other words, it means that you can use more ammonia and less bromide when developing it. For instance, in the albumen beer process with the bath\* the image is developed with strong ammonia and pyrogallie acid, and with no restrainer whatever beyond the physical restraint caused by the albumen and the iodide. It may be said the albumen alone played the part; but that is not the case; if with a collodio-bromide emulsion you use the same preservative in a similar manner, the use of a bromide in the developer becomes a necessity."

As to the use of chloride, there is much to be said for a moderate use of it. Development might be modified to suit it. We have found that using half bromide and half chloride a sensitive and beautiful picture will result when using the ferrous-citro-oxalate developer. There is no doubt, from our experiments, that silver chloride aids density, and this itself is a great advantage. We know several advanced workers who add all three haloids (iodide, bromide, and chloride) with the best possible results. Another use of chloride, as far as we know, is to allow a full dose of silver to be used to convert all the bromide present in emulsion without jeopardizing it by an introduction of free silver. Bromine displaces chlorine in the chloride of silver, when the bromine is in the form of a bromide of the alkalies, hence the addition of a certain amount of chloride is useful, even with ordinary develop-

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\* See "Instruction in Photography."



ment. It may be objected that by this procedure the bromide is not boiled in a medium which has solvent powers. This is not the case, however, as the bromide is soluble to a certain extent in the soluble chloride. It is very easy to mix a chloride emulsion with a bromide emulsion after washing, and for some purposes this is a good plan.

## CHAPTER XXV.

### COMPARISON OF THE AMMONIA PROCESSES WITH THE BOILING PROCESS.

WE will now pass on to describe comparative results of Dr. Eder's methods of emulsification by the use of ammonia, and of the boiling method.

Two emulsions were made according to Eder's first formula; the second containing about 10 per cent. of potassium iodide, and called I. and II. Two emulsions were made according to Eder's second formula, one also containing about 10 per cent. of potassium iodide, and called III. and IV.

A variety of emulsions were made and tested one against the other in many ways. We give, in a tabular form, some of the results :—

No. I.—Potassium bromide	...	...	...	93 grains
Swinburne's No. 2 isinglass	...	...	...	30 „
Nelson's No. 1 photo. gelatine	...	...	...	120 „
Water	...	...	...	2½ oz.
Silver nitrate	...	...	...	115 grains
Water	...	...	...	2½ oz.

No. II.—Potassium bromide ...	...	...	93 grains
Potassium iodide ...	...	...	10 „
Nelson's No. 1 photo. gelatine ...	...	...	120 „
Swinburne's No. 2 isinglass ...	...	...	30 „
Water ...	...	...	2½ oz.
Silver nitrate ...	...	...	127 grains
Water ...	...	...	2½ oz.

These had been made according to Dr. Eder's formula, with ammonia.

Nos. V, VI, were made with the above formulæ, but boiled with 15 grains of gelatine for half-an-hour; 105 grains of No. 1 photographic gelatine and 30 grains of Swinburne's isinglass were dissolved in 2 ounces of water, and added to them. They were each divided into two parts, and one-half of each was digested with 1 drachm of strong ammonia, as in experiments III and IV. The other halves were washed without having been digested with ammonia. All were allowed to set, and then washed as usual. Those portions of V and VI of the emulsions treated with ammonia we will call Nos. VII and VIII respectively.

Plates were coated with all the emulsions: 1st, on the same day on which the washing was complete; 2nd, on the day after, and then tested one against another. It may be convenient to call the greatest sensitiveness 10, and to show the others by lower numbers. We find the following results:—

No. VI	...	...	2nd day	...	...	10
No. VIII	...	...	2nd day	...	...	10
No. V	...	...	2nd day	...	...	9
No. VII	...	...	2nd day	...	...	9
No. VII	...	...	1st day	...	...	8
No. VIII	...	...	1st day	...	...	7
No. IV	...	...	2nd day	...	...	6
No. III	...	...	2nd day	...	...	6
No. IV	...	...	1st day	...	...	5
No. III	...	...	1st day	...	...	5

No. VI	...	...	1st day	...	...	5
No. V	...	...	1st day	...	...	5
No. I	...	...	2nd day	...	...	4½
No. II	...	...	2nd day	...	...	4
No. I	...	...	1st day	...	...	3½
No. II	...	...	1st day	...	...	3

It may be convenient to remember that the odd numbers contain bromide alone, and the even ones *iodide* with the bromide.

It will be seen, when boiling with a small quantity of gelatine (Nos. V, VI, VII, and VIII), that at the second day the plates containing iodide (VI and VIII) have a little advantage over those which contain bromide alone, and that the digestion with ammonia (VIII) gives no increase in sensitiveness. The same is apparent with VII and V; the digestion with ammonia does not increase the sensitiveness with pure bromide. The first day's plates (VI and VIII) with the iodide are in every way behind the second day's plates with the bromide alone; but evidently digestion with ammonia answers partly the same end as keeping the emulsion. The same applies also to Nos. I and II. Boiling with a small amount of gelatine, then, in every case, is better than boiling with a full quantity of gelatine, and then digesting with ammonia; but this plan is far better than digesting with ammonia alone. These formulæ are comparative ones, since they all contain eventually the same amount of bromide of silver, and the same amount of gelatine.

As regards development, the plates containing the iodide were a little slower in coming out; but, on the other hand, they were certainly much brighter and cleaner.

To test the value of the iodide further, the same formula as Nos. III and IV were used, and the emulsions brought to the boiling-point when the ammonia was present. No. III fogged; No. IV remained quite bright.

The ammonia undoubtedly makes plates much more rapid than when no boiling is attempted; the sensitiveness in which case might, perhaps, be represented as 1, but it by no means gives the most rapid kind of plate. We think for comparatively slow plates, where good density is required, Formula No. II is excellent in every way; and if anyone has a prejudice against iodide, let him use No. I.

It will thus be seen that we hold to introduction of iodide into an emulsion; except for experimental purposes we never omit it, believing it to be a sheet-anchor for obtaining good and unfogged pictures. We are aware that several commercial makers of plates which have a great name in the market use the iodide, and if those who condemn it would but give it a fair and unprejudiced trial, we should have no fear of making converts of them to its introduction.

## CHAPTER XXVI.

### GELATINE.

IN gelatine emulsions one of the most prominent features is the gelatine, and it is by no means unimportant what kind is selected. Dr. Eder has made long and exhaustive researches on various qualities of gelatine, and Mr. T. F. Elsdon has also thrown light upon its variability in an article in the YEAR-BOOK for 1881, and we cannot do better than quote some of their conclusions. Gelatine is compound of glutin and chondrin. The latter is distinguished from the former by its precipitation from an aqueous solution by acetic acid, and its insolubility in an excess of this reagent. Acetate of lead, alum, and sulphates of iron, aluminium, and copper also precipitate it; but not glutin. Mr. Elsdon also remarks that a convenient test for the presence of much chondrin in gelatine is to add a concentrated solution of chrome alum to a solution of 50 grains of gelatine in 1 ounce of water. If chondrin be present in excess, the gelatine will set whilst hot. Mr. Elsdon further says:—Remembering that gelatine is a mixture of two substances of different composition and properties, it must be expected to find great variation in the behaviour of commercial samples. Most photographic gelatines, however, consist chiefly of glutin, and their general character is not, therefore, affected to so great an extent by the small quantity of chondrin usually present in addition.

Gelatine is extremely hygroscopic, and contains, at



ordinary temperatures, from fifteen to twenty per cent. of water. In cold water it swells up, and absorbs from five to ten times its weight of water; good gelatine will absorb enough cold water to dissolve it, if the temperature is raised above  $90^{\circ}$  F. Very weak solutions of gelatine will solidify to a jelly when cold, sometimes when only one per cent. is present; but long boiling destroys, to a great extent, this power of setting.

Gelatine will keep indefinitely in a dry state; but in contact with water it soon putrefies, becoming first acid, and then strongly alkaline, and giving off ammonia; at a temperature of  $90^{\circ}$  F., decomposition will often begin in twenty-four hours. Hence it is evident that long boiling, besides destroying its power of setting, also tends to produce decomposition of gelatine.

Alum, alcohol, carbolic acid, salicylic acid, glycerine, fuchsin, hydrate of chloral, thymol, and salts of zinc act as antiseptics, preventing the decomposition of gelatine, even in small quantities. If glycerine be used, however, it must be added in rather large quantities. Alcohol and carbolic acid, in large quantities, precipitate gelatine from solution in water.

Acetic acid, hydrochloric acid, sulphuric acid, and oxalic acid dissolve gelatine even in the cold.

Acetic acid dissolves gelatine with great facility, whilst ammonia acts as a weak solvent.

Sugar promotes the solubility of gelatine, whilst gum, in the presence of acetic acid, renders gelatine less soluble, owing to the formation of a compound of gluten with arabic acid.

Silver nitrate, exposed to sunlight, in contact with gelatine, causes a red discolouration, due to the combination of organic matter with a sub-oxide of silver.

Chrome alum renders gelatine insoluble; but long boiling and hot dilute acids, potash, potassium permanganate, are able to dissolve the mixture. Alum raises the melting point, but does not render it insoluble

The quality of gelatine may be tested in several ways. Dr. Eder, amongst other tests, recommends that the gelatine be incinerated, and the ash weighed, and he says that this varies from  $\frac{1}{2}$  per cent. in good samples to 5 per cent. in inferior kinds of gelatine, and to 10 per cent. if adulterated with alum. Our own researches in this matter give a greater margin for good gelatines, 2.5 per cent. being the ash of a certain gelatine which is excellent. We detail some results in the table below. Another test which should be applied is the amount of water it can absorb. Good gelatine should absorb five to ten times its weight of water. A very simple way of testing is to measure out (say) 2 ounces of water, and soak 50 grains of the gelatine in it for some hours until it is thoroughly swelled. The water not taken up should then be poured off into a measure, the gelatine being very gently pressed against the side of the vessel in which it was allowed to swell. The amount taken up is, of course, the difference between the 2 ounces and the amount returned to the measure. A more scientific method is to allow the gelatine to take up as much water as it can at a fixed temperature, drain it, and surface dry it on blotting-paper, and then weigh it. This is a more tedious method than that given above.

Name of Gelatine	Ash, per cent.	Water absorbed by 50 grains.
Coignet's gold label gelatine ...	1 nearly ...	7 drachms
„ special gelatine ...	1 „ ...	7 „
Nelson's No. 1 photographic ...	2 „ ...	$5\frac{1}{2}$ „
„ opaque ...	2 „ ...	8 „
„ amber ...	1 „ ...	4 „
Ordinary French (not branded)	2 „ ...	6 „
Swinburne's No. 2 patent ising-		
glass ...	1 „ ...	$5\frac{3}{4}$ „
Cox's gelatine in packets ...	1 „ ...	$4\frac{3}{4}$ „
Russian isinglass ...	1 „ ...	$2\frac{1}{2}$ „
Gelatine supplied through Mr.		
Henderson ...	2 „ ...	8 „
The Swiss gelatine supplied		
through Houghton ...	2 „ ...	5 „

The next test is that of solubility. A gelatine which by itself is soluble at a low temperature is unfitted for gelatine emulsions, particularly if the temperature at which it is prepared is at all high, since it would then not set. Take, as an example of this, Nelson's No. 1 gelatine. In warm weather it will dissolve in the water at the temperature of the room in which it is soaked. Take Coignet's gold label as the other extreme, and it will be found not to melt till the vessel has been plunged into water about  $110^{\circ}$ . As might be expected, as regards setting, these two gelatines are the most opposite. At a temperature of about  $75^{\circ}$ , No. 1 will scarcely set at all, whereas Coignet's will set in a short time.

An important test is for acidity or alkalinity. For our own part we strongly recommend a gelatine which is *slightly* acid where an emulsion is to be boiled, and if not in this state, we acidify the gelatine solution. When the ammonia process is used, the condition of the gelatine does not matter so much. In some gelatines, the acidity (due to the hydrochloric acid used in its manufacture) can be tasted by applying a piece to the tongue. A hard gelatine can be at once identified when it is set after dissolving in the water, which it will absorb. Any exact determination by applying weight to see where crushing begins is misleading, unless the temperature is uniform during all experiments.

We would here remark that gelatine has an affinity for iodine, bromine, and chlorine, with each of which it combines; hence it is a preservative in the true sense of the word.

The less fatty matter present the better, since it gives rise to opaque spots on development, or else to scum-markings on the plate. Where there is fatty matter present, it may be got rid of by precipitating it in a fine stream in alcohol, or by dissolving it in the quantity of water which has to be used, and skimming it; or by making it set, and, with a clean ivory knife, cutting off a thin layer from the top.

To select suitable gelatine for an emulsion, we recommend that a small batch of emulsion be made with the specimens proposed to use, and that a few plates not smaller than 7 by 5 be coated and tested before taking it into use for larger quantities.

In our own practice we like to use a mixture of two kinds of gelatine—one hard and one soft, and the proportions of these we vary according to the weather. As a rule, we like 1 part of hard to 3 parts of soft, as it will then set with ease at a moderate temperature, and be hard enough to resist the tendency to frill; and is at the same time readily permeable by the developing solutions.

One fact must also be recollected, that frequent reheating of gelatine speedily detracts from its setting powers, and that if too little water be added to it in mixing, the film has a great tendency to become leathery, more particularly if a little chrome alum has been added to it to prevent frilling. A judicious mixture of alcohol to a gelatine solution increases permeability, and should not be neglected. The use of a sufficient quantity of water is, however, the great desideratum, and should be carefully attended to, the quantity, of course, depending on the temperature at which the plates have to be prepared; thus, in winter, more water should be used than in summer. A very horny, glassy, film is objectionable in many ways, and a matt surface for the plates should be aimed at. This depends almost entirely on the gelatine that is used, unless it be modified by additions such as glycerine, to which we may at once say we object, on account of its affinity for water.

## CHAPTER XXVII.

### GELATINO-BROMO-IODIDE EMULSION.

WE propose to give a detailed account of making an emulsion at ordinary temperatures, say up to  $65^{\circ}$  Fah., which may be taken as a pattern on which to form others by any other formula. It will be found to be exquisitely sensitive to the blue rays, and very slightly to the yellow, which latter quality means that the development and preparation of the plates can be conducted in a room with any quantity of orange light. To prepare the windows for this, the ordinary window panes may be coated with such a material as Thomas's ruby varnish paper, which will be found quite sufficient protection; though if direct sunlight beat on the window, it is desirable to have a blind of orange paper or calico, which subdues the light, since the blue rays from a very strong light might pierce the first paper if there are any deficiencies in the varnishing. Ruby glass and such a screen or curtain is a certain protection, and is convenient, since there is no danger of any change of colour in the former through the action of light or by any chemicals that may be used. A combination of pot-orange or stained red glass, which admits about the same rays, would answer equally well. The dyes made up in varnish, as given at page 30, may also be substituted. The ordinary dark-room windows, if covered

with red tissue paper such as is supplied for fancy decorations, will render the light safe. The reader must remember that tricks cannot be played with the light of the dark-room, such as are admissible when the comparatively slow wet process is used. Thus he should see that no light of the wrong colour penetrates at any place; he should pay particular attention, for instance, to the chinks under the door, and in the sashes of the window frame. When he has come to the conclusion that no daylight is entering his room, he may think about preparing the emulsion. First of all he must make a few preparations. The jar or bottle in which the emulsion has to be mixed must be scrupulously clean. There should be no patches of old emulsion left on it. If a glazed jar be used, it should be seen that the glaze is not cracked in any way, since fog may be expected if it be. For dissolving the gelatine, &c., we like to use glass beakers with a lip, since they are handy for pouring. These also must be scrupulously clean and dry. The scales in which the weighing has to take place should be examined for dirt (chemical or otherwise), and a few circular filter papers on which to weigh the materials should be at hand. Weighing should never be done\* without a filter paper of equal size and weight being placed in each pan of the scale. A saucepan of hot water should be ready in which to place the beakers, &c., in which the different materials have to be dissolved, and care should be taken that it is not too full. It need scarcely be said that all weighing can be done in ordinary light. To commence operations, the following may be weighed out separately and placed on clean† paper after weighing, it being

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\* Especially on brass scale pans.

† Any contamination by dirt of any description, and particularly that to be found in a photographer's work room, is almost sure to spoil the emulsion, or at all events its sensitiveness, and to cause endless evils. Hence *clean* paper should be used, and the chemicals should not be left on the benches or table in contact with the wood.





## ERRATA.

At page 139, after the different weighings, it is said "Nos. 1 and 2 are rapidly covered with water." It should read "Nos. 3, 5 and 6 are rapidly covered with water." And in the fourth line below, instead of "They are then dissolved in 1 dr. and  $1\frac{1}{2}$  ounces of water," it should read "Nos. 1 and 2 are then dissolved in 1 dr. and  $1\frac{1}{2}$  ounces of water."

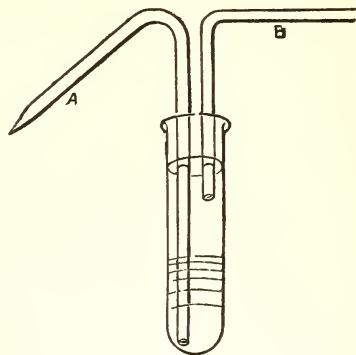
supposed that a dozen or a few more whole-plates are required.

1.—Potassium iodide	...	...	10	grains
2.—Ammonium bromide...	...	...	140	"
3.—Nelson's No. 1 photographic gelatine	...	...	30	"
4.—Silver nitrate...	...	...	200	"
5.—Nelson's No. 1 photographic gelatine	...	...	80	"
6.—Simeon's Swiss gelatine, or Coignet's special gelatine	...	...	80	"

Nos. 1 and 2 are rapidly covered with water, shaken or stirred in it a few seconds, and the water poured off as quickly as possible. This gets rid of any adherent dust on them. They are then dissolved in 1 dr. and  $1\frac{1}{2}$  ounces of water (ordinary tap water is good enough), respectively, and then No. 3 is added to No. 2, and allowed to swell in the liquid. It may require a little coaxing to get it beneath the surface of the water; but if a good-sized developing cup be used there will not be much difficulty. When swollen, the cup containing the salts and the gelatine is placed in boiling water for a few minutes, till the latter is dissolved (which it will readily do in a very short time), and raised to the temperature of about  $150^{\circ}$  F.; if the gelatine be alkaline, 1 drop of hydrochloric acid may be added (see Chap. XXXIV.) The silver No. 4 meanwhile is also dissolved in  $1\frac{1}{2}$  ounces of water slightly warm.

This last may be placed in a spray apparatus, which is made as follows:—Bend two thin glass tubes in a common fish-tail burner of the shapes A and B (fig. 11). The tube A should first of all be drawn out so that the end is perfectly closed; this may be done by the heat of a Bunsen burner, by holding the straight tube over it at about an inch from the end, in one hand, and at any convenient distance in the other, and, when thoroughly softened by the heat at one point, by simply pulling the

tube outwards. The glass collapses, and the short bit is pulled off. A flat file is then applied to the point, and the glass filed away till a very small orifice is left. The two tubes are then inserted in a cork which is fitted into a test-tube as shown. The silver nitrate is placed in the



*Fig. 11.*

bottom of the tube, and a very fine spray of liquid can be forced through the orifice of A.

The solution of gelatine and bromide should be placed in a glass beaker or a jam-pot, and in the dark room the spray is blown on to it, and the liquid stirred, at the same time, with a clean glass rod. When the silver nitrate has been added to the bromide the iodide is dropped in with stirring, and the remainder of the silver solution subsequently added. This is a better plan than adding it to the bromide at first, and depends for its value on the fact that the iodine from the iodide will replace the bromine from the silver bromide, soluble bromide being re-formed; grains of silver iodide thus formed have the same size as the bromide originally formed. This gives a very fine emulsion indeed, and, if correctly carried out, a drop of it, when poured on a strip of glass, should show an orange-yellow colour by transmitted daylight, or a deep ruby

when a gas or candle flame is examined through it. The possible sensitiveness of an emulsion depends almost entirely on the fineness of grain of the bromide when first formed. With a grey or blue-tinted emulsion extreme rapidity can never be hoped to be attained. The emulsion should be transferred to a 20-ounce bottle\* and *well shaken* for a couple of minutes, after which it is ready for the next operation.

*Other Methods of Mixing.*—There are other methods of emulsifying which are given here. Mr. England finds that if two 1-drachm measures be filled, one with the bromide solution, and the other with the silver nitrate solution, and then be poured into a bottle together and well shaken, and this operation be repeated again and again till the two solutions are exhausted, he gets a perfect emulsion without grain and very smooth. It will be noticed that in this plan the silver and the bromide solutions are in equal quantities. Another plan, adopted by Mr. Warnerke (whether it is original with him is not of great consequence) is to draw out two funnels to fine points, and support them on funnel-holders over a jar. These are filled with the two solutions, which are allowed to run into the jar, a stirrer being used to aid emulsification; other workers use the scent-diffuser, by which to secure fineness of grain. Any of these artifices may be employed. A later plan which the writer has adopted, and which is very effective, is to shake the gelatine containing the bromide into a froth, and then to add the silver nitrate little by little. This makes a beautifully fine emulsion, and seems to be equivalent to immersing a delicate film of gelatine into a silver bath, when we know that splendid films are to be obtained, having the very finest grain.

*A Reversed Mode of Mixing.*—We have quite recently experimented with pouring the bromide solution into the

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\* Some recommend the use of an earthenware bottle, such as an old ink-bottle. There seems to be no advantage in it if ordinary precautions be taken for keeping out the light.

silver solution. At first we adopted the mode indicated above, of dissolving the bromide with the gelatine. After some experimental work, we found that the silver might be mixed with the gelatine, and then the bromide added. The method gives most beautifully fine emulsions of the orange to ruby colour, which is such a desideratum. The method of mixing is as follows:—

A.—No. 1 (see p. 139) is dissolved in 1 dr. of water.

B.—No. 2 is dissolved in  $1\frac{1}{2}$  ounce of water, and the hydrochloric acid dropped into it if required (see p. 139).

C.—No 3 is dissolved in  $\frac{3}{4}$  ounce of water.

D.—No. 4 is dissolved in  $\frac{3}{4}$  ounce of water.

In the *dark room*, C is added to D, and shaken up in a bottle till a perfect mixture is secured. B is then dropped in little by little, and shaken up after each addition, and finally A is dropped in. We have never met with any red fog or other disease induced by this mode of mixing, and we recommend it in preference to the other modes indicated above.

A *good Stirring-rod* may be made by taking a glass rod, and tying across it with clean string a strip of glass about a couple of inches long and half an inch wide. This cross-piece effectually stirs up the emulsion during its formation by a motion of the rod between the first finger and thumb. We recommend its use.

*Boiling the Emulsion.*—A saucepan of sufficient size to hold the bottle must be procured, and filled with water to a convenient height, and a flame, such as a gas-burner, placed beneath it.\* After the water has been brought to boiling point, the emulsion is kept boiling for twenty minutes to half-an-hour; it being shaken at intervals (say once every ten minutes) for half a minute or so. A thick cloth tied round the hand prevents any scalding. The boiling, by-the-bye, should take place without the

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\* To prevent bumping and breaking the bottle, we place half-a-dozen folds of blotting-paper at the bottom of the saucepan.



cork being left in the bottle, for if it remain in, it would be blown out by the force of the steam. A cork with a slot cut in it is, however, not open to objection.

*Cooling and Washing the Emulsion.*—After the proper time of boiling, the saucepan is removed. The gelatines Nos. 5 and 6 should, in the interval, be rapidly rinsed in several changes of water to get rid of any adherent dust. They should then be placed in a pot with 2 ounces of cold water and allowed to swell. After this they are melted at a temperature of about  $100^{\circ}$ , by immersing the pot or flask in hot water, and added to the solution in the bottle. *Both the emulsion, and also the dissolved gelatine,* should be cooled to about  $70$  to  $80^{\circ}$  F. by allowing water from the tap to run over the jars before the addition is made.

After a good mixing by shaking, the froth is left to subside, and the emulsion is poured out into a flat porcelain dish,\* and allowed to rest. The time which it will take will vary according to the temperature of the surrounding air, but a couple of hours is generally amply sufficient, and often a much less time will suffice.† After a proper consistency is obtained (such consistency being that the gelatine should not tear with a moderate pressure of the finger), the emulsion is carefully scraped off the bottom of the dish with a strip of *clean* glass, and transferred to a piece of very coarse canvas which has been previously boiled in hot water to get rid of any grease or dirt. The emulsion is then twisted up in this, and, by a gentle pressure, squeezed through the interstices, the ball of emulsion being absolutely below the surface of the water

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\* There is no "fetish" in a dish. When the emulsion is to be squeezed, if it is set in a beaker, it turns out in a more convenient shape. In a dish, however, it sets more rapidly, since a greater surface is exposed to the cool air.

† In very hot weather, if the dish be stood in iced water, no difficulty in setting will be found. See subsequent chapter for particulars of preparing emulsion at high temperatures.

into which it is forced. The water causes the threads of gelatine to remain tolerably separate, and, as it passes through the liquid, most of the soluble salts are at once extracted.

When all is squeezed through, the particles of gelatine may again be transferred to the canvas, and, after stretching it loosely over the mouth of the jar (emptied of water), may be doused with water from the tap or from a water jug. After a couple of gallons have been thus passed over it, the emulsion should again be squeezed through the canvas, and the same operation repeated, thus exposing fresh surfaces of gelatine to the action of water. After another sluicing with water the emulsion may be considered as washed, though, to make assurance doubly sure, the gelatine may be left at the bottom of the jar, and the water changed two or three times. To show the importance of thorough washing, the following experiment may be noted. An emulsion was made as above, and after once squeezing through the canvas, a part was immediately used for making plates. A second part of the same was washed under the tap for five minutes; a third part was squeezed and washed a second time; and a fourth part was allowed to soak, and squeezed a third time. The relative sensitiveness of the four parts was as follows:—

$$1 - 1\frac{1}{2} - 2\frac{1}{2} - 2\frac{1}{2}$$

The first washing increased the sensitiveness to one and a-half, and the second squeezing to two and a-half, whilst the third squeezing and washing had no perceptible effect.

The writer considers this method of washing superior to that given below. Two squeezes, it is believed, are equal to twenty-four hours' such washing. Gelatine is hard to permeate, and, being a colloidal body, the crystalline salt has hard work to get through when the emulsion is not finely broken up.

*Other Modes of Washing the Emulsion.*—There are several modes of extracting the soluble salts from the emulsion. Putting on one side dialysis as introduced by Mr. King, owing to its tediousness, we pass on to the most ordinary method. The emulsion when prepared is poured out into a flat dish in a very thin layer (say) of about  $\frac{1}{8}$  of an inch thick. When set, it is scraped off the dish with a piece of glass, and transferred to a jar or bottle in strips. Mr. England first scores it over with the prongs of a silver fork, so breaking it up into fine strips. Cold water is then poured on to it, and a stream of running water kept flowing over it for twelve hours, more or less.

The writer has converted a tin canister into an effective washing apparatus, as shown in the figure. In the lid of

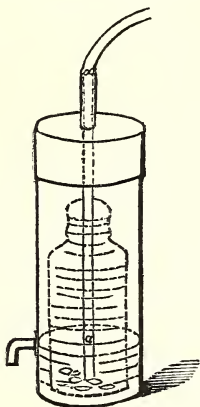


Fig. 12.

a common canister a hole is perforated so as just to admit of the insertion of a glass tube *a, a*; a piece of india-rubber tubing connects this with the water tap, and covers any small chink between the glass and the lid, as shown. A spout is soldered on to the canister, as shown. A bottle containing the emulsion to be washed is placed in the canister, the tube being inserted in it. The water

flows over the top of the bottle, and rises in the canister to the level of the spout, where it trickles over into the sink ; the heavy water containing the soluble nitrate is thus perpetually stirred up and caused to flow over the neck of the bottle. This answers admirably, and can be used in the daylight, if necessary, but is more applicable to emulsion that has been cut into strips than to that which has been squeezed twice, as the small particles are apt to be carried over the top of the bottle and choke the exit tube. A combination of this method with that given on page 143 can, however, be made by only once squeezing the emulsion through the napless canvas.

Another method is also due to Messrs. Wratten and Wainwright, and is as follows :—After the emulsion has been allowed to rest for two or three hours, two ounces of alcohol to each ounce of water used are poured into the bottle containing it, and well shaken up. The gelatine rapidly assumes a pasty appearance, and subsides to the bottom. The bottle is then inverted, and the fluid, which contains the soluble nitrates and excess of water, is poured off, and may be preserved for distillation. The explanation of the efficacy of this method is, that the alcohol has a greater affinity for water than has the gelatine, and that in extracting the water the soluble salts are extracted with it. Methylated spirit not containing gum may be used, and the lower the specific gravity the more effectual it is.

Dr. Eder, to whose careful researches photographers are much indebted, finds by absolute analysis that emulsions passed through fine canvas are sufficiently washed in about thirty-five minutes in running water, and nearly in the same time in standing water ; through coarse meshed canvas in one and a-quarter hours in running water, and in a much longer time in standing water. When cut in strips, it is probable that twelve to twenty-four hours may be necessary to free it sufficiently from the soluble salts, in order to obtain a maximum sensitiveness.

*Draining the Emulsion.*—When the emulsion is considered to be properly washed, it is then drained. This the writer generally does over the canvas, though some recommend a hair sieve, but it does not appear that there is much advantage to be derived from its use. The great point in either case is to drain long enough. A couple of hours is sufficient time, and then the emulsion is ready for melting.

It will sometimes happen that no amount of draining over a hair sieve or canvas will render the emulsion sufficiently free from water to set well when dissolved up. We have found that by pouring a couple of ounces of alcohol through the emulsion when draining that the excess of water is taken up, and it becomes firm. It should be noted that before re-dissolving the gelatine it should be firm and free from all sloppiness (if such an expression may be used); one dose of alcohol generally effects this, and, if not one, two will. The alcohol may be saved if required. In case this artifice be resorted to, only half the quantity of alcohol given before should be added to the emulsion, when it is re-dissolved for filtering and coating the plates. Emulsion that is cut up into shreds is much more easily drained than that which is squeezed through canvas. It is not that the gelatine takes up more water, but that the water clings mechanically to the small particles forming it. We recommend that the canvas be as coarse as possible, having a mesh not less than one-eighth of an inch, if such can be procured.

*Dissolving the Emulsion.*—After draining, the emulsion should be transferred to a clean jar or jam-pot, and then placed in boiling water till all the gelatine is thoroughly dissolved. A temperature of  $120^{\circ}$  or more may be given it with advantage. The emulsion, when all additions are made, will be about  $6\frac{1}{2}$  ounces. The addition of  $\frac{1}{2}$  grain of chrome alum is to be recommended. This should be dissolved in 1 drachm of water, and added with stirring; 6 drachms of absolute alcohol are next to be added in the

same way, and the emulsion is then ready for filtering. This operation may be carried out in various ways. The writer now uses wet chamois leather or swansdown calico, which has previously been well boiled and washed. This is allowed to rest loosely in a funnel, and the emulsion filters slowly through it, all coarse particles being left behind. A small plug of washed wool is used by many, and answers well. It is preferable to filter into a Florence flask, as it will bear heat, though an ordinary medicine bottle will answer if the flask be not at hand. The bottle or flask is again placed in water at a temperature of  $120^{\circ}$ , and the next operation is to coat the plates.



## CHAPTER XXVIII.

### BENNETT'S GELATINO-BROMIDE PROCESS.

THE next process we shall describe is that brought out by Mr. C. Bennett, and was the first process published which gives extreme rapidity. His description of it is extracted from the *British Journal of Photography*. Sensitiveness is attained by slow digestion at a low temperature instead of by boiling. Mr. Bennett, after describing the light required for the preparation of the plates, on which we have already written (Chapter IV.), says:—

“To make ‘assurance doubly sure,’ use a ruby-coloured hock bottle, and with two eight-ounce decanter-shaped bottles made of test-tube glass to stand heat, weigh out for a ten-ounce solution—

Ammonium bromide	...	...	70 grains
Best silver nitrate	...	...	110 „
*Gelatine	...	...	200 „
Distilled water	...	...	6 ounces

Use Nelson's ‘No. 1 photographic gelatine,’ for with the

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\* It will be noted that the gelatine and the silver nitrate have the proportion of twenty to eleven, or nearly two to one. In the bromo-iodide emulsion of the previous chapter, the proportion is four to five, supposing the gelatine in which the emulsion is boiled is destroyed. In developing it is evident the former will require less restraining than the latter.

opaque sixpenny packets you have irregularity, red fog, and frilling. Place aside four ounces of water for the bromide, and two ounces for the silver; dissolve the bromide with heat in one of the test bottles in one or one and a-half ounces of water; pour into the hock bottle; swill out the test-tube with the remainder of the four ounces set aside for the bromide, and also pour in. I do it by heat to ensure all being dissolved, as it does so very slowly after the gelatine is inserted. The four ounces of solution being now almost cold, add the gelatine, shake up well, and place in two or three gallons of water at  $90^{\circ}$ . I use a fish-kettle with lid. [A good-sized saucepan with a lid answered perfectly with the writer.] In two hours the bromized gelatine will, after well shaking, be quite liquid, and also nearly at  $90^{\circ}$ . Now dissolve the silver in the other test bottle, to be kept in one ounce of water, cool to  $90^{\circ}$ , and pour in; use the remainder of the two ounces set aside for the silver to swill out, heat to  $90^{\circ}$ , and pour in. By being so particular we get regularity, and are able to mix the plates of different batches, which is a great boon. Shake the emulsion very briskly, and replace in the kettle for two, four, or seven days, according to rapidity required. The temperature should never be over  $90^{\circ}$ ; if you do not let it exceed that, you will not have red fog. 'Cosy' it up with flannel, and it will not lower many degrees during the night. I, however, use a stove two feet across, and place it on that; a faint gas jet below keeps it always at  $90^{\circ}$ . I shake up every twelve hours. If washed in two days, the emulsion is rapid and dense; in four days, more rapid and less dense—quick enough for any drop-shutter known, when developed as below. With some that I kept for seven days, with drop-shutter, on a dull February morning, pebbles close to the camera were perfectly exposed. The negative was thin under ammonia, but bore intensifying to any extent.

“Cool the emulsion in a bottle not smaller than a Win-

chester quart, and wrap it up in brown paper to exclude all light except the lip of the neck. Let an india-rubber tube go quite to the bottom of the bottle to stir away those layers of water which, on account of greater specific gravity (by reason of the salts they now contain), would otherwise remain there. Wash for twelve hours; a dribble is sufficient. Upon melting you have eight or nine ounces of emulsion; add three-quarters of an ounce of pure alcohol heated to  $90^{\circ}$ ; fill up with water (also warm) to ten ounces, and coat. The plates should be only lukewarm, or you will have red fog. For beginners it much helps the coating to double the quantity of alcohol, leaving out water to that extent. The operator should not be alarmed at the peculiar mottling of the film (due to the alcohol) directly after coating; this subsides in a few seconds to an even surface. The extra alcohol does not appear to alter the sensitiveness, and is a great help; but with experienced workers it is not necessary, and the quantity is sufficient to draw the emulsion up to the edges, which is the sole object of introducing it. When no alcohol is used you always have *thin* edges, which is very objectionable, as the negative, of course, will print dark at those parts, and this small addition of alcohol totally rectifies this fault. It is difficult to measure the exact quantity of emulsion required for each plate; one ounce would probably cover *eight* plates of  $6\frac{1}{2}$  by  $4\frac{3}{4}$  size."

## CHAPTER XXIX.

### PAGET PRIZE EMULSION.

THE following is the description of the process sent in by Mr. Wilson, which won the Paget Prize Competition in 1880 :—

To make a pint of emulsion—

Select a 20-ounce narrow-mouth stoppered bottle, with a well-fitting stopper, and thin bottom. Make it perfectly clean.

Make a stock solution of—

Hydrochloric acid (pure)	...	1	fluid drachm
Hopkin and Williams' "Pure"	1150	ordinary	
Distilled water...	...	12½	ounces

Put into the 20-ounce bottle—

20 minims of the above *dilute* acid.

3 fluid ounces distilled water.

210 grains ammonium bromide.

(Hopkin and Williams' or Schering's, dry.)

80 grains Nelson's No. 1 Photo. gelatine.

Leave the gelatine to swell for (say) fifteen minutes or longer.

*The Addition of a Trace of Hydrochloric Acid* to the soluble bromide and gelatine is recommended in formula given,

for the following reasons:—If the soluble bromide be absolutely neutral, and the gelatine a suitable sample (see page 139), the hydrochloric acid is *not necessary*, and better omitted. If, however, the gelatine be ever so little alkaline, or even apparently neutral, but yet does not give a clear solution, acid is required. Its use is not to produce silver chloride, but to ensure a fine precipitate of silver bromide. According to Mr. Wilson's experience, a fine precipitate is hardly at all a question of the method of mixing, and elaborate contrivances for the purpose he considers as quite unnecessary. A fine precipitate is easily obtained, however rapidly the solutions be mixed, if two conditions exist, viz., if the bromized gelatine solution contain a trace of hydrochloric acid, and the *silver* solution be not stronger than 110 grains per ounce. If it be 50 to 60 grains per ounce, it may be poured all in at once; or if a little weak solution be first poured in, the stronger may follow (as per formula). A good test for the suitability of a gelatine is to see if a fine precipitate can be obtained without having to add hydrochloric acid. Too much hydrochloric acid retards or prevents the conversion of the silver bromide into the sensitive form in cooking; a large excess destroys the gelatine.

It will thus be seen that the addition of hydrochloric acid must be made *intelligently*, according to the other materials accessible.

It might be supposed that any acid would make the precipitate fine, and that, therefore, acid ammonium bromide would be good. Such is not the case, and, moreover, the acid bromide has in some way a powerful effect in retarding the conversion of the silver bromide into the sensitive form.

*Ammonium Bromide* should be as nearly as possible *neutral*. It is usually more or less acid, even though otherwise pure, and frequently becomes strongly acid by keeping. It is then quite unfit for use, and will not give good results unless almost neutral.

Since sending in the formula for competition, Mr. Wilson has arrived at the conclusion that, on the whole, it is better to use bromide of potassium. The latter is often alkaline, but may, without much difficulty, be obtained neutral, and is free from tendency to alter.

*Silver Nitrate* is usually—if good—slightly acid with excess of nitrate acid. It may be so used; but it was recently found that better results are obtained if the silver solution be neutralized with carbonate of soda. A slight excess does no harm, as the resulting trace of carbonate of silver is converted into bromide; indeed, an emulsion *may* be made by mixing washed carbonate of silver with a soluble bromide.

The uses of neutralizing the silver are twofold. One is, that as the amount of acidity of silver nitrate varies with different samples, it ensures the same conditions in all cases; the other is, that the presence of nitric acid in an emulsion produces a tendency to green and pink discolourations in the finished negative.

In another clean glass vessel (beaker, measure, or flask) dissolve 330 grains nitrate of silver (re-crystallized) in 3 ozs. distilled water.

Pour out about 2 fluid drachms of this silver solution into another small vessel (say test tube), and dilute it to half strength with an equal quantity of distilled water.

Take the 20-ounce bottle and the two lots of silver solution into the dark room. The writer prefers to use a large paraffin lamp, protected by one thickness of ruby and one of dark orange glass, to two thicknesses of dark orange paper without any ruby.

In the dark room have a gas-boiling stove, and on it a tin pot or saucepan deep enough to contain the bottle when the lid is on. It should have a tin perforated false bottom, to prevent the bottle resting immediately on the true bottom; or a piece of wire gauze will answer. Let the pot contain some three or four inches in depth of *boiling* water.



Turn out the gas of the stove if alight, and plunge the bottle into the water two or three times, so as to avoid cracking it by too sudden heating; then leave it in for a few minutes, until gelatine is completely dissolved. Do *not* leave it in longer than necessary for complete solution. Take it out, shake up, remove the stopper, and set bottle down on table near your lamp, so that you can see what you are doing.

Pour in *all at once* the four drachms of *dilute* silver solution. Put in the stopper and shake up thoroughly, but not too violently, for about half-a-minute. Now pour in the strong silver solution in quantities of about half-an-ounce at a time, shaking as before after each addition, and, when all is added, give a final thorough shaking for (say) a couple of minutes.

*If the instructions have been so far accurately followed, there will be no coarse precipitate or grit in the finished emulsion.*

Now put the bottle into the pot of hot water, see that the stopper is not jammed in, and put on the lid. Light the gas, and boil up as quickly as possible. If the water was previously boiling, and the gas only turned out for the mixing operation, it should boil up in less than five minutes; then keep boiling for *fifty-five minutes*. At the end of this time turn out the gas, take off the lid, take out the bottle, and remove the stopper *at once*, or you will not get it out afterwards. The bottle must now be cooled down as quickly as is consistent with safety to the glass. In very cold weather it may stand on the table for ten minutes or so, and then be cooled with water; or, in any weather, place it in a pan of nearly boiling water, and cool gradually by allowing cold water to trickle slowly in, shaking the bottle occasionally. Whatever method is adopted, it should be down to 90° F., or lower, in fifteen or twenty minutes at most. It cannot easily be made *too* cold, as the gelatine has lost its power of setting.

In a glass beaker (about 12 or 14-ounce size) put 1 ounce of Nelson's No. 1 Photo. or "X opaque" gelatine, and pour over it 10 ounces of clean ordinary water. Leave it to soak until the gelatine has absorbed 4 ounces of water, pour off the surplus 6 ounces, melt the swelled gelatine by immersing the beaker in hot water, and pour it into the 20-ounce bottle containing the cooled emulsion. Shake up well, and pour all back into the beaker, draining out the bottle thoroughly. Leave it to set in a cool place. Mr. Wilson prefers to leave it for twenty-four hours. It has next to be washed.

*The Addition of the Gelatine* after boiling should be made when the boiled emulsion and dissolved gelatine are *both* at as low a temperature as possible, and between the time of this addition and that of washing the emulsion, it should be kept as cold as possible. The reason of this appears to be that the excess of alkaline bromide has a most destructive effect on the new gelatine, and therefore the lower the temperature and shorter the time during which the two are in contact the better.

There is a curious effect depending on the temperature at which the emulsion and fresh gelatine are mixed, viz., that if quite cold the resulting plate will have a matt surface, and the higher the temperature the more glossy it will be.

A plain solution of gelatine in pure water is very little injured by prolonged boiling; but if an alkaline bromide (or chloride) be added, it is speedily decomposed. Probably the alkaline nitrate, which is present in the emulsion in large quantity, may be even more effective.

For the washing, clean ordinary water at a temperature *not over* 50° F. should be used. The writer prefers *at all times* to use water cooled down to below 40° by melting ice in it. By so doing uniform results are obtained, and where ice can be procured the cost is trifling; 3 lbs. of ice will be sufficient for a pint of emulsion in the hottest weather.

In a glazed earthenware pan or other suitable vessel, put about 3 pints of cold water, and add 3 ounces of saturated solution of bichromate of potash (made by saturating clean ordinary water with bichromate, Hopkin and Williams' re-crystallized).

Before squeezing the set emulsion through the canvas, it should be cooled down so as to be as firm as possible. If so, the water into which it is squeezed will remain almost clear, or but slightly milky. If the *emulsion be soft*, even though the *water* be ice cold, the water will be more milky, and the emulsion take up too much. Too much excess of acid bromide, too high a temperature at the time of adding the gelatine, or keeping at too high a temperature between adding and washing, will produce the same result.

The emulsion may, of course, be washed by precipitating with alcohol, squeezing the clot, breaking it up, and soaking in water; but the writer prefers washing with water and bichromate, as described, on account of the clear and brilliant shadows so obtained.

Having cooled the beaker of set emulsion down to 40° F., run a bone spatula or paper knife round and turn out the emulsion, or cut it out in lumps. If cold, it will come out almost quite clean from the glass. Place it on a piece of coarse "straining cloth" or canvas, and squeeze through the meshes into the water, the operation being performed under the surface of the water. Leave it so for an hour. Lay the straining cloth over the mouth of another pan or large jar, and pour the mixture of emulsion threads and liquid on to it so as to let the latter run through. Squeeze the emulsion a second time through the cloth into clean cold water, and immediately repeat the operation a third time, leaving the emulsion in the last water for half an hour. When strained for the last time, place cloth and all in a large beaker, and put the latter into hot water until the emulsion is completely melted and warmed to about 115° F., *i.e.*, not warmer than is pleasant to the

hand. With a *clean* hand take out the cloth and squeeze it; very little will be lost. The emulsion should now measure about 16 or 17 ounces. Add 2 ounces alcohol, and mix thoroughly. The alcohol may be either pure ethylic alcohol, sp. gr. about .830, or *good colourless* methylated. The writer prefers the former. If the emulsion now measures less than 20 ounces, make it up to that by adding clean water.

A good deal depends on the temperature at which this is done, and by careful management much may be effected. If the emulsion is sufficiently rapid and free from pink and green disease, it is best melted and coated at a low temperature. If it be slow and has a tendency to colour, it will be improved by heating to 140° F. Mr. Wilson has had emulsions which became *more than three* times as rapid by this treatment; but it is a somewhat dangerous one, as too high a temperature, or too prolonged heating, may result in hopeless grey fog. This kind of fog is more apparent during development than after fixing.

The emulsion is now ready for use. It should be filtered into the coating cup through cotton-wool to free from bubbles, and plates coated in the usual way, dried and used as usual for rapid gelatine plates, using about an ounce of emulsion for a dozen quarter-plates.

In drying arrangements, avoid the contact of gas or of the products of combustion of gas with the moist plates. The writer finds both to be very injurious.

*Exposure.*—As usual for good rapid gelatine plates—say Wratten and Wainwright's "instantaneous."

*Development.*—Either pyrogallic, ammonia and bromide, or ferrous oxalate. If the former, sufficient exposure and as little ammonia as possible will give best results.

## CHAPTER XXX.

### BURTON'S PROCESS.

MR. BURTON has quite recently worked out a process which certainly simplifies the washing of an emulsion, but which at the same time is rather more expensive, in that it requires the use of spirits of wine or methylated spirit for precipitation purposes. Mr. Burton has kindly forwarded a statement of his process, and we give it as he has described it. He prepares the following solutions:—

1.—Silver nitrate	...	...	...	212 grains
Water	...	...	...	1½ ounces
2.—Ammonium bromide	...	...	...	120 grains
Ammonium iodide	...	...	...	10 „
Gelatine (Nelson's No. 2 photo-graphic)	...	...	...	30 „
Hydrobromic acid	...	...	...	1 drop
Water	...	...	...	1¼ ounces

These are emulsified as given in Chapter XXVII., at page 140, or by shaking in a bottle as described at page 141. There is no reason why the precipitation should not take place by the reversed method (page 141), and we recommend it.

The emulsion is boiled as given at page 142, and is then allowed to cool to about 50° or 60° F. It is then poured



in a stream into 6 to 10 ounces of alcohol, the quantity depending on the specific gravity of the spirit used; 6 ounces of absolute alcohol suffice, whilst it is safe to use 10 ounces with ordinary methylated spirit, since it usually contains a large quantity of water. The emulsion settles down to the bottom of the vessel in a few seconds in the shape of a dense flocculent precipitate. Most of the soluble salts are, of course, at once extracted, but it is better to wash it further, either by decantation, or by placing it on a hair-seive in running water; the precipitate is coarse enough not to pass through the meshes.

In the meanwhile the following has been prepared and made into a solution:—

Nelson's No. 2 gelatine	...	120 grains
Autotype or Swiss hard gelatine	150	"
Water	...	12 ounces

The bromide of silver precipitate is added to this, and well shaken till it is dissolved and all granularity has disappeared.

The difference between this process and that originally described by Wratten and Wainwright (see page 146) is, that in the one case the emulsion containing all the gelatine is precipitated, and in the other but a small quantity of gelatine has to be thrown down, and consequently the elimination of the soluble salts in the latter case is far more perfect. There is also a saving in alcohol. To prepare an emulsion in the shortest possible time, this process meets the requirement, since it saves much time in washing, and all the time of draining.

Again, too, it will be seen that this is a capital plan of preparing dry pellicle which will keep indefinitely, and the bromide will remain in its most sensitive condition, since, after precipitation and washing, it will rapidly dry, as the bulk of gelatine is so small, and is in a granular state.

Mr. Burton recommends the use of acid, as it gives what



he happily calls a "robust character" to the emulsion ; that is, that the plate will stand more rough usage, and more forcing in development. The larger amount of gelatine recommended by Mr. Burton allows alkaline development almost unrestrained by bromide to be employed, and at the same time is no doubt economical in a pecuniary point of view ; at the same time, there is no reason why the quantity of gelatine recommended in Chapter XXVII. should not be used, in which case the water should be reduced to 7 ounces.

## CHAPTER XXXI.

### DR. EDER'S PLANS OF PREPARING GELATINE EMULSIONS WITH AMMONIA.

ONE of these methods is based on the utility of allowing ammonia to re-act upon the bromide of silver in its original condition, which enables the sensitive emulsion to be formed more rapidly than by Monckhoven's method. The second method, by which greater sensitiveness is obtained, consists in boiling the gelatine emulsion by itself, and subsequently treating it with ammonia at 95° F. for half an hour. We quote Dr. Eder's own words (see *Photographic Journal*, November 19, 1880).

I. *Method with Ammonio-Nitrate of Silver.*—This method furnishes very sensitive plates, which are at least six or seven times as sensitive as wet plates. The necessary operations are simple and quickly executed, requiring but few apparatus and arrangements, and may be effected without continued warm digestion, a shaking-up arrangement, a light-tight cooking-pot, and so on. The requisites are an ordinary cooking-pot, a spirit lamp, a thermometer, and a reliable dark-room. The plates show great power and density, and keep wonderfully clear. The emulsion works so clean, and is so free from granulation, that not only landscapes and portraits can be taken with it, but reproductions of linear drawings can

be made without intensification. The following is the formula he recommends:—

No. 1.—Potassium bromide	...	370 grains
Gelatine ...	... 520 to 700	„
Water ...	... 10½	ounces

This is dissolved (as given at page 139) and raised to a temperature of from 95° to 120° F.

No. 2.—Silver nitrate	...	460 grains
Water ...	... 10½	ounces

Into this latter is dropped strong liquor ammonia till the precipitate is just re-dissolved, and it is then, in a ruby light, added drop by drop to No. 2, and shaken. The flask containing the latter solution is rinsed out with 1½ ounces of water, and the emulsion is then placed in a water-bath at a temperature of 95°, for from a quarter to half-an-hour, gradually allowing it to cool down to 75°, but not lower.

The salts and the gelatine do not require to be so carefully chosen for this method as for that which follows. Should the bromide of potassium have an alkaline reaction it does no harm in this method; neither is the neutrality of the nitrate of silver imperative, nor the acidity of the gelatine; indeed, it may be alkaline.

The specific gravity of the ammonia, regarded as a determinant of its strength, is a secondary consideration. Take a strong solution of ammonia. The proper quantity is defined sharply enough by the sign—"as much ammonia as will re-dissolve the precipitate produced in the nitrate of silver solution." As one is deprived of this indication by which to regulate properly the addition of ammonia, whenever one adds the ammonia to the gelatine containing bromide of potassium (instead of to the nitrate of silver), Dr. Eder does not so much recommend this manner of mixing, though, by the alteration in the procedure, the same sensitiveness is obtained as by

the former method.\* Great care should be taken, when adding the ammoniacal silver solution, that the temperature does not rise too high, and that, during the digestion, the water-bath does not become too hot, otherwise fog is sure to result. The temperature should never exceed 105° F.

When the digestion is finished, the emulsion should be poured into a glass beaker (one made of not too thin glass) or into a porcelain dish, which is placed in cold water to accelerate the setting. When set it is pressed through canvas as used for Berlin-wool work, and the operation may be conducted as given at page 143, and then washed in frequently-changed (or, better still, running) water for twenty-four or forty-eight hours, whilst suspended in a coarse stuff bag. A great deal of water adheres to the gelatine particle, which should be allowed to drain for at least half-an-hour, either from the bag or else through a cloth filter placed loosely in a large funnel. If this draining be omitted, the emulsion will most likely be too fluid. The superfluous water may also be removed with advantage by gentle pressure.

The finely-divided emulsion may either be deprived of water by placing it in a bath of alcohol, and then dried in thin films in the air, either perfectly or only superficially,† or it may immediately be liquefied by heating in the water-bath. Filtration through flannel placed in a warm funnel is good; but it is generally sufficient to allow it to deposit any sediment by standing quietly at rest. If it be intended to keep the dissolved gelatine emulsion for some time, an antiseptic must be added. To 10 ounces

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\* When gelatine, bromide of potassium, and ammonia are dissolved, and the nitrate of silver is then added, the ammonia should not be allowed to act too long upon the gelatine. The ammonia is best added immediately before the addition of the nitrate of silver to the gelatine.

† Dr. Eder stated that he had not tested this method so minutely as to be able to maintain that it furnishes exactly the same product as an emulsion immediately re-dissolved; but that he finds this preparation keeps better than the dissolved aqueous emulsion.

of emulsion add 10 grains of salicylic acid dissolved in 1 drachm of alcohol, or replace the salicylic acid by the same weight of thymol oil, as a protection of the gelatine against change caused by long warming, putrefaction, &c. The alcohol has a favourable action, accelerating the setting of the gelatine and the drying of the film.

The proportion of bromide of potassium to nitrate of silver is 4 : 5 ; it is not advisable to take less bromide, as one would run the risk of fog. The difficulty of fixing the proportion of the soluble bromide to the nitrate of silver consists in finding the proper medium between the too much bromide, which retards the sensitiveness, and the too little, which it is not possible to overlook, on account of the decomposition of the bromide of silver which sets in, both in the case of treatment with ammonia, and boiling. The proportions mentioned are those which have been found best both by Captain Toth and Dr. Eder.

The conversion of the insensitive modification (which transmits red light) into the extremely-sensitive modification (transmitting blue light) takes place in a very short time when the above directions are followed. Even at a temperature of 25° C. (77° F.), the complete conversion generally takes place in from fifteen to twenty minutes. A small sample poured as a thin film on a sheet of glass is sufficient to test whether the rays transmitted, whether of daylight or of naked gas or candle-light, are blue or not. In the former case the digestion may be ended. Generally, the prolongation of the digestion over thirty minutes develops no further increase in sensitiveness worth mentioning; but if the temperature be not raised above the point before mentioned there is, even after three hours' digestion, no danger of fog.

If the liquid be too hot, or the solution too thin (that is to say, too poor in gelatine), or if the added ammonio-nitrate of silver be dissolved in too little water, the bromide of silver will be too coarse in the grain. It then quickly settles at the bottom, and the emulsion becomes

unequally mixed. The negatives also would be coarse-grained, but there would be, nevertheless, no particular increase observable in the sensitiveness.

By the gentle heat prescribed above, the gelatine should not be injured or changed that its setting power, &c., should suffer. It is, therefore, intentionally recommended to add all the gelatine at once. By all methods of emulsification with ammonia the separate addition of part of the gelatine after the digestion is ended is impracticable, since the greater part of the gelatine must be added before the setting and washing, in order to impart the necessary solidity to the mass, and a renewed heating of the emulsion in order to dissolve the additional gelatine would be unavoidable. The repeated or too prolonged heating of gelatine emulsion containing ammonia, as is known, is hurtful.

The emulsion must be washed with great care. It is quite impossible to attain the full sensitiveness of the plates in the presence of any considerable quantities of soluble bromide; besides which, the slight residue of ammonia is an enemy to the keeping qualities of dissolved emulsion, because, even in small quantities, it has a corrosive action, and combines with the salicylic acid, subsequently added as an antiseptic, to the great injury of its property of retarding putrefaction.

II. *Method by Boiling and Subsequent Digestion with Ammonia.*—This is more complicated than Method I., and requires more care. It is based on the observation that the modification of bromide of silver which transmits blue light is produced very rapidly at a temperature of from 60° to 100° C. (140° to 212° F.), and that the sensitiveness of such an emulsion—already of itself highly sensitive—can be increased by subsequent treatment with ammonia at a gentle heat, while continued boiling would bring fog.

The proportions of the separate ingredients are the same as in Method I. (see page 163). The emulsion is



then boiled; but during the boiling the cork should not usually be driven in quite tight, for fear of the bottle being shattered by the expansion of the steam. When using a common glass bottle, change the ordinary cork for one which has a groove cut in it. The bottle filled with emulsion is put in a perfectly light-tight tin saucepan furnished with a tight-fitting lid,\* and under the saucepan is placed a gas jet or a spirit lamp, care being taken that not even the reflected light from the spirit flame should fall upon the emulsion. Of course it is understood that the whole operation takes place in the dark room. The boiling is continued for half an hour from the time the emulsion reaches 100° F. (see page 143).

The emulsion already possesses a high degree of sensitiveness (similar to that of the best commercial gelatine plates), and may be used without any further treatment with ammonia. The latter, however, increases the sensitiveness. When the emulsion has become quite cool (the temperature may fall to 70° F.), add to it two drachms of ammonia, s.g. .880, place it in a water-bath of from 95° to 100° F., and digest at this temperature for half-an-hour to an hour. At the end of that time the emulsion is ready, and one then proceeds, after it has set, to wash it, &c.

During the subsequent treatment with ammonia care must be taken that the temperature never exceeds 105° F. Generally, digestion for half-an-hour suffices, but with an hour one is surer of having attained the desired sensitiveness. Even digestion for two hours does not develop fog. The prolongation of the digestion with ammonia is particularly useful when the previous boiling is interrupted before the bromide of silver is sufficiently modified. It is assumed, however, that during the whole process of digestion the water *never sinks below*

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\* A linen rag laid at the bottom of the saucepan prevents the bottle from cracking in consequence of coming in sudden contact with the hot metal forming the bottom of the pot.

100° F. All the precautions described as applicable to the adding of ammonia (Method I.) also apply here.

Here also all the gelatine must be added at once; it does not do (as in Method I.) to retain a portion of it and to add it later. Dr. Eder, however, expressly mentions that with very easily-affected sorts of gelatine one may be in a position to add part of the gelatine when the digestion is completely ended.

With regard to other details (washing, quantity of gelatine, &c.), the remarks made with reference to the last method apply here.

Dr. Eder says a gelatine emulsion prepared by Method II. is more sensitive than one prepared by Method I. The difference is, perhaps, not extremely great, still the sensitiveness of that prepared by the Method II. ought at least to be a fifth greater than by Method I. It gives negatives with good gradation, and free from that hardness which is often seen in less sensitive emulsions which are difficult of reduction by the developer. The whole picture generally comes out pretty quickly under the developer, and, even when the exposure is very short, the shadows are sufficiently densely developed before the lighter parts have become too intense. Dr. Eder believes this emulsion will be found particularly suitable for portraiture in the studio. It can be worked to opacity, but is less apt to produce perfectly white or black negatives than emulsion prepared by the first method.

To sum up in a few words :—Emulsions prepared by Method I. are most suited for the production of hard negatives, and those prepared by Method II. for soft negatives. The former has the same character as the most sensitive emulsions at present in the market; the character of the latter is unusual. *Still it cannot be said that with either, both hard and soft negatives cannot be got according to the way they are developed.*

In the preparation of emulsions by Method II. great care must be exercised. The gelatine and bromide of potas-

sium should not have an alkaline reaction, for fear of the formation of fog during the boiling. The materials must, therefore, be previously tested with litmus paper.\* If the nitrate of silver be added to the gelatino-bromide of potassium, when heated to 60° or 70° C. (140° to 160°F.), the formation of the extremely-sensitive modification is sooner produced.

The ferrous oxalate developer is especially suited to these fairly sensitive gelatine emulsions, though the alkaline developer may also be used; the former gives particularly clear and brilliant negatives.

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\* Should one not be able to obtain any neutral or slightly acid preparations, the hot solution of bromide of potassium and gelatine may be carefully acidified with dilute acetic acid or hydrochloric. The reaction should be only *slightly acid*, otherwise the acetic acid will destroy the setting power of the gelatine.

## CHAPTER XXXII.

### A COLD EMULSIFYING PROCESS WITH AMMONIA.

MR. HENDERSON has experimented on what may be called the lines of Dr. Eder: viz., with ammonia, but using the full quantity of gelatine. Mr. A. Cowan, however, has made a modification which, we believe, has not been published, and this we give as certainly the easiest form of the ammonia process, and, so far, we have proved it to give the best results as regards rapidity.

The same proportions of gelatine, bromide, iodide, and silver are taken as given at page 139, and dissolved up in the same amount of water. The silver should be dissolved in cold water, and the gelatine solution, after dissolving, should be cooled. This can readily be effected by making the vessels containing the different solutions to stand in cold water. To the silver, however, is added sufficient ammonia (equal parts of ammonia .880 and water) just to dissolve the oxide first formed. The bromide and gelatine are then gradually added to the ammoniacal silver nitrate, and a fine emulsion is formed. The remaining gelatine is dissolved in the same amount of water as given at page 143, and its solution also should be cooled down. This is added to the emulsified bromide, the two are well shaken up together, it is then poured out and set without

further treatment, and washed in the usual manner. If the emulsion be kept a day, it will be found to have great sensitiveness.

The success of this method in giving sensitiveness shows that the sensitive form of bromide formed by ammonia is quickly arrived at in a but slightly viscous fluid, whereas it is not fully formed until a quarter to half-an-hour has elapsed (and even then not unless the solution be rendered less viscous by warming), when the full quantity of gelatine is employed. There is one thing that has struck us in using the emulsion, viz., the large number of plates that can be coated with this quantity of emulsion—nearly double, in fact, of those that can be coated by the emulsion formed as given in Chapter XXVII. The gelatine, too, becomes softened, and it is sometimes advisable to add in a dry state 40 grains of hard gelatine to the emulsion when washed, and before making up. The above quantity will coat forty  $7\frac{1}{2}$  by 5 plates.

## CHAPTER XXXIII.

### A PROCESS FOR GELATINE EMULSION-MAKING IN HOT WEATHER.

THE method adopted is very similar to that described in our last chapter, but there are one or two alterations in procedure. In the first place, we use the following formula, which is the same as that given there, except we substitute potassium for ammonium bromide. It is as follows:—

Potassium bromide	...	...	250 grains
Nelson's No. 1 gelatine	...	...	45 „
Water	...	...	1 ounce
Strong hydrochloric acid	...	...	2 drops

This is prepared in the usual way, and warmed up to 120° F., and the following added as given at Chapter XXVII.:—

Silver nitrate	...	...	300 grains
Water	...	...	3½ oz.

Finally to this is added—

Potassium iodide	...	...	12 grains
Water	...	...	1 drachm

The emulsion is then transferred to a glass flask, and boiled for three-quarters of an hour, shaking up the emulsion at intervals. This is allowed to cool in the flask for half-an-hour, when to it is added, after dissolving and cooling—

Nelson's No. 1 gelatine	...	...	120 grains
Coignet's, or Swiss hard gelatine	...	...	120 „
Water	...	...	3 oz.



The emulsion is poured out into a jam-pot, which is immediately placed in iced water with a few lumps of ice floating in it. In half-an-hour the gelatine will be firmly set. The gelatine is loosened from the sides of the jam-pot, and the lump of emulsion is transferred into moist canvas, and squeezed through into a jar of iced water (the water having been run through filter-paper to get rid of all floating matter) in which a few small lumps of washed ice are floating. After ten minutes the water is changed, and after another ten minutes is changed again, when it is again collected in the canvas, and squeezed through into water. One more change of water should be sufficient to free it from all except traces of soluble salts. It is then transferred to the canvas, and allowed to drain over a jar for half-an-hour to three-quarters (see p. 147).

It is again transferred to the jar-pot and melted, and two or three drops of carbolic acid (or other antiseptic) added, and then once more placed in iced water. In half-an-hour it is set, when it is covered with alcohol and allowed to ripen for a day; and if the jar be placed in water containing a lump of ice, so much the better. When plates have to be coated, the slab on which the plates have to be set is covered with small lumps of ice for half-an-hour, and if it be thick it is only very gradually cooled; but, on the other hand, it also only very gradually gets warmed again. During this time the emulsion is melted, six drachms of alcohol, one grain of chrome alum in one drachm of water added, and filtered. When the plates are coated (after the slab has been dried from all water), it will be found that the film of emulsion will set in a couple of minutes, and that the slab remains cool enough to enable five or six batches of plates, each batch filling the slab, to be prepared; that is, supposing your slab to hold eight plates, you can coat forty to forty-eight without re-cooling the slab. The gas of the drying-box may be lighted immediately, and the drying of the plates will proceed rapidly, and not re-melt. If gelatine be once *well*

*set*, it requires a high temperature to re-melt it; and the more the water is evaporated, the higher the temperature required. As the current of warmed air passes over the plates the moisture is rapidly absorbed, and hence the drying can be effected with safety.

Supposing by any chance the emulsion appears too thin before coating the plates, 40 grains of Coignet's gelatine may be melted in three drachms of water and added to the emulsion, with much stirring, immediately before filtering.

It may be said that there is nothing novel in this way of proceeding. It, however, contains a feature which has not been much practised, the value of which was first practically pointed out by Mr. W. B. Bolton. He recommends hydrobromic acid instead of hydrochloric. He prepares a solution of this acid (s.g. 1.45) in distilled water 5 parts, or hydrochloric acid 1.20 to 5 parts of distilled water. Before boiling the emulsion, he adds a couple of drops of one of these mixtures to the emulsion, and tests from time to time for acidity by means of test-paper. By this means the free ammonia resulting from the decomposition of the gelatine is neutralized, and thus fog is prevented. This plan of adding the acid may be used in the method detailed in Chapter XXVII.; but it is not so necessary in it as during hot weather, since at the temperature at which the gelatine sets in ordinary weather the action of ammonia is not rapidly deleterious. If the gelatine be alkaline in hot weather, even when set, decomposition quickly sets in. This is the reason why the hydrochloric acid is added; and since decomposition sets in more easily in the liquid state than in the gelatinous state, this is the reason why it is set by means of acid. The alcohol is used during the ripening to prevent the access of air to it.

## CHAPTER XXXIV.

### GELATINO-BROMIDE EMULSION MADE WITH GLYCERINE.

THE next emulsion is one described in the *Photographic News* by the writer. It is a method of preparing an emulsion by adding *washed* silver bromide to gelatine.

Let us suppose we are going to make up about 7 ounces of gelatine emulsion. Weigh out ammonium bromide, 140 grains (or its *equivalent* in zinc, potassium, or any other bromide), and dissolve in 20 ounces of water (not necessarily distilled water). Next weigh out 250 grains of silver nitrate, and dissolve in 6 ounces of water, and add 6 drachms of glycerine to it, and stir thoroughly with a glass rod. We prefer to put this mixture in a glass jar holding about 40 ounces (an empty French prune bottle would answer every purpose).

The bromide solution should now be added very cautiously. Take a 10-ounce measure, and fill it up to six ounces, or thereabouts, so that it is not too full, and gradually drop, little by little, the solution into the silver solution, stirring very thoroughly the whole time. A milky emulsion forms, and gets thicker and thicker till the whole bromide in the 20 ounces is added, though, of course, the fluid is *per se* thinner; a quarter of an ounce of nitric acid is next added, and well stirred up.

This addition is made to save any chance of fog, which might be caused by the excess of silver present. The reason of this has already been described in Chapter I.

This emulsification is better carried on in a dark room, though it is not absolutely necessary. *The bromide solution must be poured into the silver solution, and not vice versa, or a failure will be most probable.* The glass jar and its contents may now be placed away into a cupboard, and left for as long a time as is convenient, but not for less than a quarter of an hour. By the latter time the silver bromide will have fallen to the bottom of the jar, with the exception of a very *slight* milkiness, which will subside in a couple of hours. The silver bromide, however, left in suspension at the end of the quarter of an hour is so small that it may be decanted off without detriment to the emulsion. The jar may be tilted, and the liquid poured off, or a syphon may be introduced (and this is a neater way), and the liquid syphoned off close to the precipitate. About 20 ounces of water are again poured into the jar, the precipitate *well* stirred up, and again allowed to subside. As soon as ever the subsidence takes place, the water is again decanted or syphoned off. This operation is repeated four or five times, after which the decanted water may be tested for acidity, and for silver nitrate.

To try for the former, moistened litmus paper is held over an open ammonia bottle till it is thoroughly blue, then well washed in distilled water; this is thrown into the decanted water. The faintest trace of acid will redden it. If it does turn red, the washing must be repeated. To test for free silver nitrate, add to the wash water 1 drop of potassium chromate. A red colouration indicates the presence of silver nitrate. In case of the presence of either one or the other, as is shown by the litmus paper and the chromate, the washing must be continued.

The next part of the process has now to be taken in hand. 100 grains of gelatine are soaked in 2 ounces of

water; this 100 grains should be Nelson's "No. 1 photographic gelatine," and another 100 grains of harder gelatine, such as Coignet's gold medal or Swiss hard gelatine in 3 ounces of water. The vessels containing both these (after the gelatine is properly swelled) are placed in warm water of about  $100^{\circ}$  Fahr., which will gradually dissolve up the glutinous masses. This effected, the smaller lot is placed in a wide-mouthed bottle capable of holding about 20 ounces of fluid, and the washed silver bromide added to it. The mouth of the bottle is then closed by a cork or bung, and the contents well shaken up until it becomes a froth. It is next placed in a kettle or saucepan containing warm water of about  $100^{\circ}$  Fah., and the latter is held over a Bunsen burner or spirit lamp to keep up the temperature. When the froth has subsided, the bottle is again shaken, and the warming process repeated. After two or three such shakings a little of the gelatine emulsion may be dropped upon a glass plate, and examined for granularity. If absent, so much the better; but if present, half the second lot of dissolved gelatine must be added, and the shaking repeated.

If the emulsion be raised to boiling (as at page 142) for five minutes, then shaken, and the same operation repeated a second time, we believe that an emulsion is obtained which, for rapidity, will bear comparison with any other process. This plan will give as smooth an emulsion as any other method, provided the operator's fingers are not all thumbs when the bromide is dropped into the silver.

When the emulsion is ready, the remainder of the gelatine solution not already added should be poured into the bottle, together with half an ounce of alcohol, and after a final shake, and filtering through washed cotton-wool, it is ready for coating the plate.

It is more difficult to emulsify silver bromo-iodide in this way, and the more tedious method of washing the gelatine emulsion should be resorted to.



## CHAPTER XXXV.

### DR. VAN MONCKHOVEN'S PROCESSES.

*1st Process.*—Dr. Van Monckhoven, in trying the writer's original plan of washing the silver bromide before adding it to the gelatine, failed, but hit upon the following ingenious methods, which are given in his own words:—

“I prepare very pure and dilute hydrobromic acid, and I determine accurately the amount of it required to precipitate exactly 150 grains of silver nitrate. I then dissolve this quantity of acid in 7 ounces of water, with which I incorporate, by heating, 40 grains of gelatine. On the other part—and from this moment I entirely operate in the dark room—I precipitate 150 grains of silver nitrate by a very slight excess of bicarbonate of soda; I let it settle for twenty-four hours, and then renew the water to the same amount, after which I let it settle again previous to decanting. On this precipitate of silver carbonate I pour a hot solution of 30 grains of gelatine in 7 ounces of water. This is well stirred, and then I pour on it the solution of gelatine and hydrobromic acid. The mixture is thoroughly shaken every quarter of an hour, and is kept at the constant temperature of 120° Fahr. The silver carbonate dissolves slowly in the hydrobromic acid, and the silver bromide is formed in the colloidal liquid in a state of extreme sub-division. At



the end of ten or twelve hours the mixture, when flowed over glass plates, has a greenish white colour. I next introduce 150 grains of gelatine, cut into very thin shreds, which I dissolve by stirring, and then, without washing the emulsion, I flow it over the glass plate.

"In order to obtain a success with this method it is necessary to take some precaution. The hydrobromic acid must be free from phosphorus and sulphur; the water used for washing the silver carbonate must contain no trace of carbonic acid.

"In an emulsion prepared by this method there is always an excess of hydrobromic acid and of silver carbonate, but I have satisfied myself by other experiments that the presence of these substances does not affect the results. This is not the case if carbonate be replaced by the oxide of silver; the emulsion is then grey, and gives rise to fogging. The plates that I have prepared by this method are twenty times as rapid as the best wet collodion, and, compared with the best English plates, I have found them to be three or four times as rapid. For the rest, the same observations and the same methods apply also to collodio-bromide."

*2nd Process.*—Dr. Van Monckhoven's second process is as follows:—

"Procure some of Nelson's No. 1 photographic gelatine. I insist upon this point, because you will not succeed with German or French gelatines, which are prepared in a different manner from those of Nelson. Weigh up exactly 153 grains of this gelatine and 122 grains of pure and well-dried ammonium bromide. Put these two substances into a bottle, and pour upon them 10 ounces of distilled water. In a quarter of an hour the gelatine will have swollen, and you can now put the bottle into a warm water bath and agitate, in order to dissolve the two substances.

"Weigh out 184 grains of silver nitrate, and dissolve in  $1\frac{3}{4}$  ounces of distilled water. Now pour the silver

emulsion into the bottle containing the bromide, a little at a time, well shaking it after every addition. When all the silver solution has been added, pour in 1 drachm of pure ammonia of a density of .880, and shake up well the solution. The ammonia exercises quite a special action here; its effect is to render the emulsion ready to be used in a few minutes, or, if great sensitiveness be required, it can be obtained in a few hours instead of days, and thus decomposition of the gelatine is avoided.

"Now pour the solution of gelatine into a porcelain dish, and place it upon cold water, and let it set. When set, detach it from the dish, place it in a strong linen sack, and wring it so that the gelatine is expelled in shreds, which are easily washed through a fine sieve. A washing of five hours in water three times changed suffices. Collect the pellicle on a clean linen cloth, and dissolve it at a temperature of 35° Centigrade, and it is fit for use. This process is a combination of those of Mr. Bennett and Messrs. Wratten and Wainwright, with this difference—that I add the ammonia in order to have the emulsion ready to work in a few hours instead of days."

## CHAPTER XXXVI.

### COLD EMULSIFICATION WITHOUT AMMONIA.

Mr. COTESWORTH has just described a plan of gaining sensitiveness by allowing an emulsion to gain sensitiveness by remaining liquid at ordinary temperatures. We recollect that a somewhat similar proposal was made of emulsifying at a low temperature in gum-arabic. Following out Mr. Cotesworth's general directions, we have arrived at fairly satisfactory results. An emulsion is prepared, as far as the boiling operations, according to Chapter XXVII., the reversed mode of mixing (page 141) being preferred. An emulsion which has a beautiful ruby colour, if kept liquid, will, in 24 hours, have attained a grey-blue colour. A comparison with Bennett's process (Chapter XXVIII.) will show that the difference between the two processes is, that Mr. Cotesworth uses very little gelatine for emulsification to begin with, whilst Mr. Bennett uses the full quantity. The consequence is that the latter gentleman was obliged to have recourse to prolonged emulsification at about  $95^{\circ}$ , in order to overcome the viscosity of the gelatine, whilst the former can get sensitiveness in twenty-four hours at (say)  $60^{\circ}$  F.

In cold weather we have found it necessary to add a couple of ounces of water to the sensitizing emulsion, in order to prevent setting. In this case the extra gelatine required is added dry, and, after soaking, the emulsion is warmed, and the gelatine melts.

There is nothing different in the preparation or development of the plates to call for any special remark.

## CHAPTER XXXVII.

### PREPARATION OF THE PLATES.

*Cleaning the Plates.*—Now, there is something to say as to the mode of cleaning plates, since a good emulsion is often condemned for frilling when the glass plates are, in reality, at fault. It is our own practice to immerse the plates in nitric acid and water (1 to 10), then to wash, and next to rub them once with a 10 per cent. solution of caustic potash or soda and a little methylated spirit. After a wash under the tap the water should flow quite evenly from off them, when, after a rinse with distilled water, they may be set up to dry, which they will do very rapidly if allowed to stand on clean blotting-paper. Polishing a plate is a mistake; it only encourages the formation of blisters, as it prevents the adhesion of the film to the glass. Avoid French chalk, or anything but pure water, and then one of the causes of frilling and blistering will have been eradicated. The plates having been cleaned as above, they are brought into the dark room, which should, if possible, be kept at a temperature between  $50^{\circ}$  and  $65^{\circ}$ , as this is the heat which is most convenient at which to coat the plates and to ensure setting.

*Substrata.*—If it be determined to use substrata to avoid

frilling (for which it is a perfect cure) the following formula (Mr. Forrest's) may be used :—

White of egg	...	...	...	1 ounce
Water	...	...	...	20 ounces
Methylated spirit	...	...	...	1 ounce
Carbolic acid	...	...	...	20 drops

The carbolic acid is added with stirring to the spirit, and then the mixture poured into the albumen and water which has been previously mixed.

Dr. Vogel gives another substratum, which is also efficacious and easily applied :—

## I.

Gelatine	...	...	...	50 grains
Acetic acid	...	...	...	$\frac{1}{2}$ ounce

are placed in a bottle and warmed till solution takes place. This keeps a month.

## II.

Chrome alum	...	...	...	10 grains
Water	...	...	...	$\frac{1}{2}$ ounce

is next prepared.

Take of No. I	...	...	...	$2\frac{1}{2}$ parts
No. II	...	...	...	1 part
Methylated spirit	...	...	...	70 parts

and filter; coat the plates after cleaning and drying as with collodion, and allow the substratum to dry.

We have used a stronger solution, and found it also to give the required result :—

Gelatine	...	...	...	50 grains
Acetic acid	...	...	...	$\frac{1}{2}$ ounce
Alcohol	...	...	...	$\frac{3}{4}$ ounce
Chrome alum solution	...	...	...	1 drachm

This is applied like collodion, and gives a beautifully

bright, transparent film. It can be "dried off" against the fire, or over a Bunsen burner.

One ounce of water-glass to 8 ounces of albumen and 8 ounces of water is also to be recommended. Plates are washed, and whilst wet coated with the above solution, which is poured off and allowed to dry. After drying, the plates are again well washed and dried. The substratum given at page 78 also answers perfectly.

*Levelling Shelf.*—The next point to look to is the shelf on which to lay the plates after coating. In our own practice we have a piece of thick plate glass about 3 feet long by 1 foot broad, and  $\frac{3}{4}$ -inch thick.\* We level by means of three mahogany wedges and an ordinary spirit level.

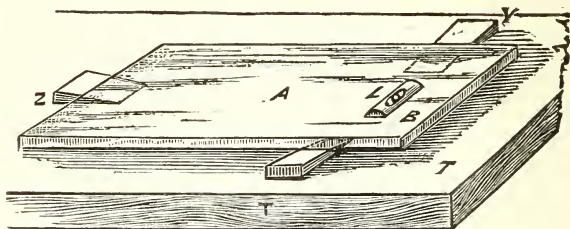


Fig. 13.

The level L is placed first across the plate, and the two wedges X and Y are altered till the bubble B of the level is central; the level is then turned lengthways along the plate, and the bubble caused to occupy its proper position by shifting Z, not touching X or Y. This should cause the plate, if true, to be accurately level; but it is as well to repeat the operation. A couple of supplementary wedges are sometimes useful if the glass "spring" at all.

*Coating the Plate.*—The shelf being level, a plate is taken on a pneumatic holder, or held upon the tips of the fingers. We will suppose the plate is of the  $6\frac{1}{2}$  by  $8\frac{1}{2}$  size that is to be coated. About 2 ounces of emulsion are poured into a

---

\* A ground slate slab answers equally well.



warmed measure, *taking care that no bubbles are formed* (which can be secured by pouring out the emulsion against the side of the measure), and a pool of gelatine is made at the top of the plate. It is then, by careful pouring, made to fill up the centre of the plate, and flow to the right-hand top corner, next to the left-hand top corner, then to the left-hand bottom corner, and, finally, to the right-hand bottom corner, where it can be partially poured back into the measure. The amount used should be noted; about 3 drachms should be sufficient to well cover the plate. The plate is then detached from the pneumatic holder (if used), held by the two corners of the diagonal, and quietly rocked till an even coating is seen to be secured. It is then cautiously slipped on the level shelf, and left to set. Another plate is taken and similarly treated; and when the shelf is full, the emulsion on the first plate will have set, and it must be removed to the drying-box or cupboard.

There are other modes of coating the plate to which we may refer. After a central pool is formed on the plate as above, the emulsion may be guided by a glass rod along each edge, and thus the chance of spilling is lessened. For our own part, we think that this is not a good plan; first, because the glass rod is liable to collect dust, as it must be wiped between coating each plate; and secondly, if the central pool of emulsion be not spread out rapidly, coating marks are apt to be seen on the finished negative.

Another plan which is advocated is to brush the plate over with a very thin film of emulsion by means of a wide badger-hair brush (kept in a small quantity of warm liquid emulsion), and then to pour over the plate the full quantity. This is not a bad plan if the brush be kept clean. If resort must be had to any methods, our preference would be to use a ruler rather larger than the plate, one edge of which is covered with swansdown calico, or chamois leather. This should be dipped into a long narrow trough of emulsion and swept along the surface of the plate, and

then the emulsion poured on immediately afterwards. No doubt with plates to which a substratum is given some such artifice is almost necessary.

*Level Cupboard-shelves.*—Instead of a levelling shelf as given above, it is perfectly feasible to alter the cupboard shown at page 22, and the alteration does away with the drying markings sometimes found, and due to the iron wires. The wires are removed, and glass or slate strips substituted for them. For plates  $8\frac{1}{2}$  by  $6\frac{1}{2}$ , slips 3 inches wide are sufficient, and they should be a  $\frac{1}{4}$ -inch thick to prevent bending. One end of the slip is supported in a stirrup shown in fig. 14, in the top of which is a slot,

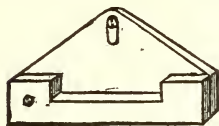


Fig. 14.



Fig. 15.

through which a screw is passed into the cupboard ; opposite to this is another stirrup (fig. 15), into which are inserted two thumbscrews as shown. This is placed exactly opposite the first stirrup in the cupboard. The strip is placed between these two stirrups, and is first levelled crossways by means of the thumbscrews. When level in this direction the length of the strip is levelled by raising or lowering the first stirrup, and when in position the screw in the slot is screwed home. When once levelled, the strip will always fall level into position. In our own cupboard we have seven of such strips across the cupboard, and they answer admirably. The coated plates are at once placed on these shelves, and allowed to set in the position in which they are to be dried.

It has been stated (though we have never found it so) that markings may be met with owing to the emulsion setting more rapidly in those parts of the plate which are in contact with the strips. If such should be feared, we

recommend that triangular pieces of card of  $3\frac{1}{2}$  inches size should be cut, and drawing-pins passed through them at each corner, and that these, with points uppermost, should be laid on the strips where the plates have to be placed. The setting will then take place without any chance of drying markings, since the plate will be supported by points. Drawing pins may be got by the gross, all of the same height. This plan is very suitable for warm weather when plates take long to set. The shelf in such weather often becomes filled before the plates are capable of removal to the drying cupboard.

Some dry-plate makers prefer to dry their plates in a nearly vertical position in racks, and there is no doubt that when drying takes place in this manner there is less chance of dust settling on the plates. At the same time, it must be remembered that the plates must be thoroughly set before they can be placed in this position. Drying, with coated face down, can also be carried out with a little ingenuity; but we see no special advantage in it.

*Drying the Plates.*—The temperature of the cupboard should be kept as even as possible, sudden changes being detrimental—producing markings. Opening the drying cupboard door before the plates are dry, when once the gas has been turned on, is a mistake; the plates should be left until it is judged they are quite dry. Very quick drying is a mistake, as the different layers of the film get an uneven strain which eventuates in frilling. Six hours is about the minimum time which we can recommend, unless drying by alcohol is resorted to. The temperature should, if possible, not exceed  $80^{\circ}$  F., and the gas must be regulated accordingly. Drying by alcohol is effected by placing each plate, *after thorough setting*, in a dish of methylated spirit free from resinous matter for ten minutes, when it will dry in an hour without difficulty.

## CHAPTER XXXVIII.

### DEVELOPMENT OF GELATINE PLATES WITH ALKALINE DEVELOPERS.

IN Chapter II. we have already shown the theory on which development proceeds; but here we must enter a little more fully into the matter. We have shown, when the alkaline developer is used, that *as a rule*, a restrainer, in the shape of soluble bromide, to prevent the primary reduction of the silver bromide unaltered by light, is requisite. We have italicized "*as a rule*," since, in some cases, this restrainer, which acts chemically, is really unnecessary, as a restrainer which acts physically can take its place. This was the case in the old albumen beer process, which was well known till emulsion superseded it; the iodide in the plate separates the particles of bromide one from the other, and the albumen wraps these up, as it were, in a colloidal shield, through which the solution finds its way more slowly than it would if they were unshrouded. Gelatine is also a colloidal body, and we may expect to find the same hold good; as a fact, with many plates it does, and more especially with those plates which are prepared with an emulsion containing a large proportion of gelatine,† as compared to the bromide.

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\* If we take emulsion, for instance, prepared by Bennett's process, we find that the proportion of silver nitrate to gelatine is 11 to 20; in the formula we have given at page 139 it is 20 to 16; that is, in one case the silver nitrate is about  $\frac{1}{2}$  the weight of gelatine, and in the other  $\frac{2}{3}$ ths. It can thus be easily understood how in one case no potassium bromide is required, whilst in the other a little is requisite.

With some commercial plates, for instance, where the silver bromide is minimized, alkaline development may proceed with the greatest ease without any chemical restrainer, the physical action of the gelatine being sufficient. It is for this reason that it is difficult to give any definite formula which can apply to all plates. In alkaline development, we may take it that there are three components: 1, pyrogallie acid; 2, ammonia; 3, potassium bromide.

Before proceeding further we will consider the different functions of the pyrogallie acid, the ammonia, and the soluble bromide.

The ammonia and the pyrogallie acid we will take first. As already pointed out (p. 16), pyrogallie combines with the oxygen, and the bromine from the silver combines with the ammonia. Suppose we have just sufficient of both to complete the reaction indicated, what will be the effect of increasing the one or the other?

If the ammonia be increased we have an increased energy of the pyrogallie acid for oxygen, which is to be obtained from some source or another. It may obtain it from the air, or from the ammonia by developing the image; we may conclude, then, that the two sources from whence the oxygen is obtained will be used pretty equally. Hence, increase in ammonia means increased rapidity of development. It also gives an increased amount of reduced silver which may increase density, since the pyrogallie acid will be used up to the greatest extent possible. It will also be seen that the addition of successive doses of ammonia to the developer will give the same result.

The addition of pyrogallie acid to the normal solutions means an increased power of reduction and a larger amount of oxygen to be absorbed, and consequently more silver to be reduced, but it will be reduced more slowly than where the ammonia is in excess. Now slow development, in a properly permeable plate, means density, since the silver is reduced in a coarser form, giving the



appearance of density with the minimum amount of metallic silver. It must also not be forgotten that pyrogalllic acid is *per se* an absorbent of bromine when it has no oxygen to absorb.

In a  $7\frac{1}{2}$  by 5 plate about 8 grains of silver bromide are reduced to the metallic state, and this case from about  $3\frac{1}{2}$  grains of ammonium bromide. A little calculation will show that the presence of 2 minims of strong ammonia are necessary to cause this conversion in the presence of pyrogalllic acid; and allowing for loss by vapourizing, at least 4 minims should be employed. The amount of pyrogalllic acid to effect the same may probably be placed at about 2 grains, and allowing for oxidation, by contact with the air, 4 grains at least would be necessary for the full amount of ammonia.

The bromide of potassium, or other soluble bromide, slows the development, probably through a formation of a double salt of bromide of silver and potassium, which being reduced with difficulty retards reduction, and hence a greater apparent density of deposit is given through the slower development.

The question then arises, should the pyrogalllic acid, the bromide, or the ammonia be first applied to the film? We believe that the application of pyrogalllic acid first has a slight tendency to slow the plate; but, on the other hand, it is safe to do so, and then subsequently to add the other solutions together, little by little, till proper density is obtained. There can be no doubt that flooding the plate with the bromide solution first, is wrong in principle, since bromide has a tendency to destroy the photographic image. On the other hand, the first use of an ammoniacal solution has much to recommend it, as pointed out by Colonel Wortley; it takes a minute quantity of silver bromide into solution, which, on the addition of pyrogalllic acid (and bromide if necessary), it is ready to deposit on the image, and at the same time the reduction of the photographic image of sub-bromide to the metallic state



commences. The great fear of this method, however, is a slight veil. A safe plan, perhaps, is to flood the plate first with ammonia and bromide, and then to add the pyrogallie acid. But on the whole, for a properly exposed plate, we should recommend that all three should be mixed in full proportions, and applied at the same time to the film. Wetting the plate before development is equivalent to diluting the developer, and, as a rule, is not to be recommended except in cases where there is a very horny film which requires softening, and then a slightly more concentrated developer should be used.

Development of a gelatine plate is in reality an art and science combined. The art consists in getting proper gradation, and the science in mixing your solutions to obtain it. There are only two kinds of exposed plates which deserve attention at all: one when it is exactly timed rightly, and the other when it is over-exposed. An under-exposed picture should be washed off as quickly as possible, or framed to illustrate "a horrid example."

Before accepting what has been laid down, the reader is strongly recommended to make a few experiments himself. First let him take formulæ such as the following:—

P.—Pyrogallie acid ...	...	...	50 grains
Water ...	...	...	1 ounce
B.—Potassium bromide ...	...	...	50 grains
Water ...	...	...	1 ounce
A.—Ammonia .880 ...	...	...	2 drachms
Water ...	...	...	2½ ounces

These nearly correspond to 10 per cent. solutions. Expose an 8½ by 6½ plate, and cut it by the diamond into six parts. Obtain a small dipping bath such as is used for quarter-plates, or a glass cell such as is used in physical laboratories.

The first experiment, perhaps, would be to take 20 minims of P, and add to it 1 ounce of water, place it

in the dipping bath, and then immerse the end of one of the pieces of the plate in it for one to two minutes. Take it out and pour the pyrogallie acid solution into the cup in which has been dropt 40 minims of B, and 80 of A. Develop the plate in the dish, and note the result.

Other experiments of the same type are, to use the bromide first, then the bromide and the ammonia, and then the ammonia alone. Further experiments should then be made by increasing or diminishing the proportions of the pyrogallie acid, &c., when no doubt the reader will be able to confirm what has been said of the matter, or to make his own deductions.

We now come to the development which is most suitable for any class of plates. The method the writer adopts is as follows. He uses the solutions of the strength given above, and having exposed a plate to the sensitometer (see Appendix) he develops it by taking—

P	...	...	...	...	20 minims
B	...	...	...	...	30     "
A	...	...	...	...	60     "
Water	...	...	...	...	2 ounces

These are mixed together and poured over the plate lying in a dish, and when fully developed the last number visible before fixing on the sensitometer read. This gives a correct idea of sensitiveness of the emulsion used. The number 14 on Warnerke's standard would mean a slow plate, 24 a quick plate. The plate is then fixed, and the density of the first five or six numbers noted. Suppose—

1st.—They are intensely opaque.

2nd.—They are about right printing density for a white cloud.

3rd.—They are thin.

To meet the first case, the pyrogallie acid should be reduced to 10 minims, and another plate tried. This will usually suffice to reduce the density. If not, a reduction of the bromide to 20 minims may take place, and this is

sure to be effective, care being taken, however, that this last reduction does not induce fogging, in which case the ammonia must be diminished.

To meet the next case, the strength of the pyrogallic acid solution is evidently correct ; a reduction in the bromide may, perhaps, be made. A plate should be tried by flooding it first with the bromide and ammonia solutions, and then the pyrogallic acid be added. The plates should then be thoroughly tested by a few further trials in varying the amount of ammonia and bromide.

To meet the last case, the pyrogallic acid should be increased to forty minims, and the bromide may be also increased to sixty minims ; if this fails to give density, it is very doubtful if any developer will give the required intensity, and intensification will have to be resorted to when using this batch of plates. Be it remembered, however, that a thinly coated plate is bound to give a thin image ; it is supposed that the plates which are being tried have been properly coated.

Having fixed the normal developer for any particular batch of plates, we have next to consider how to develop a negative, the exposure of the plate being unknown. The above given formula constitutes a normal developer for the emulsion described in Chapter XXVII. We shall therefore use these solutions. The writer would commence by taking—

A	...	...	...	...	10 minims
B	...	...	...	...	5       "
Water...	...	...	...	...	2 ounces

and would allow the plate to soak in this solution for a minute. It will be noticed that the solution is weak. Into the cup there should be dropped the normal strength of pyrogallic acid suitable for the plate under development, which we will suppose to be 20 minims. When the A and B are returned to the cup, the whole solution is poured over the plate, and the development watched. If

the image begins to appear immediately, the developer is flowed off and the plate rinsed, and into the cup are dropped 30 minims more of B and 20 of A ; the image will now appear more gradually, and increase in density ; 30 minims more of A and B may then be added, and it will be found that the negative will attain sufficient intensity. There should be no fogging of the plate if sufficient bromide be used ; this is a case of over-exposure. If the image begins to appear in about ten to fifteen seconds, it may be presumed that the exposure has been correct, and then the full doses of the ammonia and bromide A and B may be at once added to the cup, the developer poured back, and used till sufficient intensity is obtained.

Should the image not appear for twenty seconds, the developer should be poured away, the plate rinsed, and be flooded with A 60 minims in 1 ounce of water (supposing this to be the strength of ammonia it will bear in the normal developer) ; and after a couple of minutes 20 minims of B and 20 of P should be dropped in the cup, and development be proceeded with ; if the image appears in two or three seconds, and begins to get detail in ten, the action may be allowed to continue ; if not, 30 more of A and 20 of P should be added. If this fails to bring out detail, the plate is hopelessly under-exposed, and no amount of forcing will make it yield a good negative.

Such are the outlines of development by the alkaline method. It will be seen that there is more than "rule-of-thumb" work in it. It requires an intelligent application of the known effects of the different ingredients composing the developer to make the best of a negative. There are innumerable changes to be rung on the three compounds which make it all the more difficult to carry out properly.

A general favourite with photographers is the glycerine developer of Mr. Edwards, as described by him, and made as follows :—

Make two stock solutions, and label them No. 1 and No. 2.

## No. 1.

*Pyrogallic acid	...	...	...	1 ounce
Glycerine	...	...	...	1 „
Methylated alcohol	...	...	...	6 ounces

Mix the glycerine and spirit, and add to the pyrogallic acid.

## No. 2.

Bromide of potassium (or ammonium)	...	...	...	60 grains
Liquor ammonia, .880	...	...	...	1 ounce
Glycerine	...	...	...	1 „
Water	...	...	...	6 ounces

The above stock solutions will keep any length of time.

To make the developer, add 1 part of No. 1 to 15 parts of water, and label this bottle D (developer). In another bottle mix 1 ounce of No. 2 with 15 ounces of water, and label it A (accelerator).

It will be found convenient, to avoid mistakes, to have these two bottles of different shapes. Either of the above solutions will keep two or three days. When required for use, pour into a clean glass measure equal parts of D and A, adding the A last just before using. Place the dry, exposed plate face up in a shallow dish or tray, and pour the mixture steadily over the plate, avoiding air-bubbles. Should any adhere to the surface of the plate, at once remove them with the finger, or a camel's-hair brush kept for the purpose. Rock the dish gently, taking care to keep the plate well covered with the solution. In a few seconds the image will appear, and, if the exposure has been well timed, all the detail will be out and the development complete in about one minute, when the negative should be well washed under the tap, and placed at once in the fixing bath.

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\* The writer believes that for landscape work it is better to reduce the pyrogallic acid to  $\frac{3}{4}$  oz., as too much density is liable to be given to the highest light with the 1 oz.



Do not hurry the development, but allow the plate to remain in the solution after all the details are visible until the required density is obtained. With this developer, used in the above proportions, there is no danger of fog, except from the action of light.

If, on the application of the mixed developer, the image flashes out and the details in the shadows appear too quickly, it will indicate that the plate has been over-exposed; therefore at once throw off the mixed developer, and, without stopping to wash the plate, flood it with D alone, when the development will be checked, and will proceed more slowly, while the image gains in density; if too slowly, or the negative appears to be getting too intense, add a very little of A. There will, however, usually be sufficient of the latter left on the plate to complete the development with the simple addition of a sufficient quantity of solution D. A very little experience will enable the operator to produce a good printing negative from a plate which, if developed with the full proportion of A, would have been utterly useless from over-exposure. In very warm, bright weather, it will, perhaps, be found an advantage to use rather more D than A in the mixed developer, giving just sufficient exposure to avoid hardness in the negative. Under-exposure can be corrected to a great extent by increasing the proportions of A in the mixed developer, but the addition should be made at once before the development has proceeded too far, or the effect will be to increase the density, and cause too much contrast in the negative.

These concentrated stock solutions will be found very convenient to use, and a great saving of time in weighing and measuring small quantities.

The great enemies of this developer are the air-bells which form on the plate, and they are to be feared in all developers which contain glycerine or sugar.

To develop plates made with a large proportion of gelatine, we give Mr. Bennett's directions for development with his long emulsifying process.



He soaks the plate for a minute in water in the developing dish, and then pours the following quickly along that side of the tray which is not occupied by the plate. By rocking the dish suddenly it sweeps over the plate (it is developed in five to twenty seconds):—

Pyrogallic acid	...	...	...	1 grain
Bromide	...	...	...	<i>none</i> *
Ammonia (·880)	...	...	1 to 10	drops†
Water	...	...	...	1 ounce

He says :—Do not flood with pyrogallic acid first, or you will render the plate slower; nor add more pyrogallic, or you will again slow the plate, and, moreover, have it too dense. If the exposure has been sufficiently short, you should have a dense negative, with bare glass for shadows, almost as soon as the developer has covered it. If much ammonia be used, and the plate be not developed in half a minute, fresh developer should be made, and the plate be washed.

Mr. Henderson recommends the use of ferro-cyanide of potassium with the ammonia, and we give a formula. Some find it has a tendency to produce fog, whilst others have not found this difficulty :—

A nearly sat. sol. of potassium ferro-				
cyanide	...	...	...	10 ounces
Ammonia	...	...	...	10 drops
Pyrogallic acid	...	...	...	15 grains

He states that if this developer be kept from light and air, it retains its developing properties a long time. If it refuses to develop, a few drops of ammonia will set its

\* For reasons for this omission, see beginning of this chapter.

† The quantity of ammonia depends on the shortness of exposure and the sensitiveness of the plate. About 4 drops may be considered as the average amount required.

developing power in action. If free ammonia be present, and it still refuses to develop, then a little pyrogallie acid must be added.

Nelson's developer is made as follows :—

### No. 1.

Pyrogallie acid	...	...	1 ounce
Methylated spirit	...	...	7 ounces
White sugar	...	...	1 ounce
Distilled water	...	...	3 ounces

### No. 2.

Ammonia .880	...	...	4 ounces
Ammonium bromide	...	...	1 ounce
White sugar	...	...	$\frac{1}{2}$ ounce
Water	...	...	2 ounces

Use 40 minims of No. 1, and from 30 to 40 minims of No. 2, mixed in 2 ounces of water.

Messrs Wratten and Wainwright, with their ordinary or slower plates, recommend the following :—

I.—Pyrogallie acid	...	...	2 grains
Water	...	...	1 ounce

used freshly mixed.

II.—Potassium bromide	...	...	15 grains
Water	...	...	1 ounce

III.—Ammonia (.880)	...	...	1 drachm
Water	...	...	1 ounce

The plate is softened for one minute in water, 1 ounce of No. I. is applied for one minute, and then 3 minims of II. and III. are dropped into the developing cup, and the pyrogallie solution poured back. This is again poured on, and the image develops. When development flags, 3 minims more of No. II. and III. are again added till sufficient density is obtained.

For these rapid plates (and, indeed, for most rapid plates

to be found in the market), and also for plates prepared as in Chap. XXVII., use the following :—

I.—Ammonium (.880)	...	...	1 ounce
Potassium bromide	...	...	60 grains
Water ...	...	...	3 ounces
II.—Pyrogallic acid...	...	...	3 grains
Water ...	...	...	2 ounces

The plate is soaked in water for a minute, when the water is poured off, and No. 2 substituted. From 15 to 20 drops of No. I. are poured into the cup, No. I. returned into it, and applied again. The plate develops rapidly. For our own part we like to add No. I. at two intervals of time, as the development is more under control.

All the above formulæ are given in the simplest possible form, no additions being made. Many photographers, however, add nitric acid or citric acid to the pyrogallic acid to keep it from discolouring. When using them, however, it must be remembered that a certain amount of ammonia is thereby neutralized. If nitric acid be used, 4 minims will be sufficient to keep 60 grains of pyrogallic acid free from colour.

If citric acid about 10 grains should be used, Mr. Berkeley for the same purpose uses about 8 grains of neutral sodium sulphite to each ounce of water employed. Of all additions, we may say we prefer this last, since it has no neutralizing effect on the ammonia.

For removing the yellow colour so often seen in alkaline developed gelatine negatives, also for the use of the alum bath to avoid frilling, see the chapter on "Defects in Gelatine Negatives."

The fixing bath used will be found at page 209.

## CHAPTER XXXIX.

### DEVELOPMENT OF GELATINE PLATES WITH FERROUS-OXALATE.

DEVELOPMENT with ferrous oxalate developer is unquestionably the favourite method with the writer, though his partiality for it is not shared by a great many photographers. For purity of image and general excellence of quality he believes that no developer can be compared with it. There can be no doubt that it is more expensive than the alkaline pyrogallate developer : but not very much so, since several plates may be developed with the same quantity of developer. It must not, however, be forgotten that after each plate is developed, a considerable amount of soluble bromide finds its way into the solution, owing to the combination of the bromine liberated from the reduced bromide combining with the potassium oxalate (see page 18). After many plates have been developed, the solution, however, is not beyond use, since a few drops of a weak solution of sodium hyposulphite are most effectual in giving it fresh developing power. We will now suppose that we have a plate to develop by ferrous oxalate, and trace the manipulation from the beginning.

The plate is taken out of the slide in the dark-room (the light dependent, of course, on the fact as to whether

the emulsion has been prepared with or without iodide), and placed in a flat dish a little larger in bottom area than itself. If the plate has a glossy surface, and has been prepared with hard gelatine, we recommend that it be soaked for five minutes in ordinary water, in order to cause the gelatine to expand vertically, and so to soften the film, after which time the water is poured off. If the surface be matt, we recommend that the plate be not wetted. Two developing solutions are prepared. A saturated solution of ferrous oxalate in potassium oxalate is prepared as in the Appendix, and sufficient of it necessary to develop all the plates desired to do at one time is diluted with an equal bulk of water,\* and when the slight precipitation of the yellow ferrous oxalate has taken place, sufficient of the dilute solution to well cover the plate is poured over its surface, and watched for half a minute. If the image appears to be developing fairly well, and detail coming out, this developer is continued till all detail appears, when it is poured back into a developing cup, and density obtained with fresh undiluted solution of ferrous oxalate, to which 20 drops to each ounce of a 20-grain solution of potassium bromide are added. This gives density. The development should be continued till the image appears *well* on the surface of the gelatine next the glass plate, supposing the film to be of medium thickness. Many people recommend the dish not to be rocked to and fro; but we think it better to give a gentle motion to the liquid, as we have found that sometimes fog is induced by not doing so. The plate is next rinsed under the tap, and placed in the alum bath, made as follows:—Potash-alum, a saturated solution in water. It must not be supposed that this bath merely prevents frilling. It does more, it decomposes any calcium oxalate which may be formed by the water (containing

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\* Perhaps the best plan is, when the concentrated solution, prepared as shown in the Appendix, is made, to dilute it with an equal bulk of water before filtering. Some ferrous oxalate will be thrown down, and, of course, can be utilized afterwards.

lime) with which the developer is washed off. After a couple of minutes' immersion in this bath, it is placed in the fixing bath, and when all the silver bromide and iodide have been dissolved, it is washed under the tap, and the operations given at page 209 repeated.

Instead of the image coming out properly with the developer as indicated above, we will suppose that after a half a minute the high-lights only slightly appear. In this case, to each ounce of concentrated developer 20 drops of a solution of sodium hyposulphite made as follows are dropped into the cup, and the dilute developer poured on to the hyposulphite :—

Sodium hyposulphite	...	...	2 grains
Water	...	...	1 ounce

The mixture is once more poured on to the plate, and if not much under-exposed for the normal developer, the details should appear rapidly and with good gradation. When all detail is out the plate is washed, and the strong ferrous oxalate solution with the bromide is applied as before, to secure density.

Supposing the plate to be over-exposed, when the first developing solution is applied, the details will begin to appear too rapidly. It should be immediately poured off, and the plate flooded with a solution of potassium bromide (5 grains to the ounce of water), which should be allowed to soak into the film for a couple of minutes. It is then drained off. To each ounce of the weak solution 20 drops of the same solution may be added, and the developer applied again. This should allow the image to come up properly without flatness, but it may be desirable to finish with the strong solution as before.

It must be recollected in using this developer that the addition of potassium bromide means, in reality, the conversion of the bromide into bromide of iron, which is a stronger retarder than potassium bromide. Hence the addition of the latter should be made with caution.



Some photographers like to use old ferrous oxalate solutions, to which sodium hyposulphite is added at the commencement. This no doubt gives brilliant pictures, but is apt to cause exposure to be prolonged.

On the whole, we recommend tolerably fresh ferrous oxalate if the greatest benefit is to be obtained from the developer. The developers made by mixed solutions of ferrous sulphate and potassium oxalate (see Appendix) are not so strong as those we have supposed we are using; an allowance in exposure should be made for their weakness, if they are used. Either developer, however, can be used with the sodium hyposulphite, and the difference between their detail-giving powers is then very small.

There are some plates which are unsuited for ferrous oxalate development. They are generally those which are prepared with soft gelatine in hot weather. The film shows reticulation, and the image appears granular. In that case resort should be had to alkaline development, by which this evil will be lessened. A plate worth using, however, should always stand the ferrous oxalate development.

## CHAPTER XL.

### INTENSIFYING, FIXING, AND VARNISHING GELATINE NEGATIVES.

*Silver Intensification.*—This part of the gelatino-bromide process is one which has to be touched upon with the very greatest care, since all methods of giving intensity have as yet to stand the test of time. Now, as a rule, a gelatine negative has to be intensified *after* fixing,\* since the opacity of the film is usually so great that the operator is unaware what density his negative has taken under development. The great desideratum is a good silver intensifier, but this is fraught with so many dangers that great precautions must be taken to ensure success. It may be laid down as an axiom, that to be successful the whole of the hyposulphite of soda and silver must be eliminated from the film, and where the film is of any thickness this is by no means rapidly effected by simple washing. The writer finds after the green tint of the unacted-upon salt has disappeared in fixing, the plate should be placed in fresh hyposulphite, and kept there for a short time. This being done, the plate had better be kept in water for an hour or more, the water being changed at intervals. After this, the gelatine film may be made more secure by applying to it a solution of *peroxide of hydrogen* in water. A drachm of what is called a 20-volume solution to 5 ounces of water is

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\* As to intensification with silver before fixing, see Appendix.

sufficient. When it has soaked in this for half an hour, it is again washed, and intensification can commence. Another plan is, after thorough washing to immerse the plate in fresh alum solution for half an hour, again washing thoroughly, and allow to dry, and then the intensifying may be proceeded with. Those who may have endeavoured to intensify with pyrogallic acid and silver (see "Appendix") a negative treated in the ordinary way will find that red stains occur almost invariably where the film is thickest—that is, where the hyposulphites have not been thoroughly eliminated, and to eliminate them this extra precaution above indicated is necessary. The following is recommended:—

Ferrous sulphate	...	...	5 grains
Citric acid	...	...	10 „
Water	...	...	1 ounce

To this, one or two drops of a 20-grain solution of silver nitrate are added, and the plate intensified as if it were a wet plate. Now, it by no means follows that a film thus intensified would be free from a liability to change in the presence of light, since the silver might partially combine with the gelatine. After density has been attained, the plate is washed and put in a dish containing common salt, and once more passed into the fixing bath for a few seconds, again washed, and then dried.

Mr. Dudley Radcliffe has slightly modified the above, and he, too, recognizes the importance of eliminating the hyposulphites. To eliminate them, he places the film, face downwards, in water in a pie-dish, by which the heavier solution sinks to the bottom. He intensifies with the following:—

Sulphate of iron and ammonia	...	1 ounce
Lump sugar	...	1 „
Glacial acetic acid	...	2 ounces
Albumen of	...	1 egg
Distilled water	...	20 ounces

The albumen is added after the other ingredients are dissolved.

Success in intensifying by either of these methods the writer has found to be more certain when the ferrous oxalate developer has been used in lieu of the ordinary alkaline developer.

We have heard of failures with these methods, and when traced to their source have almost invariably found that they arise from intensifying negatives which have been exposed to the air. It is no uncommon thing to see on such an iridescent film, to which, if silver be applied, staining is certain. In this case a very dilute solution (5 grains to the ounce of water) of potassium cyanide should be applied, and, after well washing, the intensification may begin; cyanide will generally remove any red stain which may occur if the above hyposulphite destroying solutions have been applied first.

*Mercury Intensifiers.*—The next intensifiers are the mercury intensifiers, which may be classed as most uncertain in their action and in the permanency of their results. The negative can be intensified either immediately after the washing which follows the fixing, or it can be employed upon a negative which has been dried. In the latter case the negative must be steeped for a minute or two in water. Mr. England recommends the following as giving him what he desires:—

Mercuric chloride (bichloride of			
mercury)	...	...	... 20 grains
Ammonium chloride	...	...	... 20 „
Water	...	...	... 1 ounce

After the negative has been thoroughly washed, the above solution is poured over it till the surface assumes a grey tint. After a thorough wash (see page 209) a weak solution of ammonia (10 drops to 1 ounce of water) is applied till a dark tone is assumed by a reflected light, and brown by transmitted light. With collodion the intensity

thus given is unstable, and the film has a tendency to bleach.

To Mr. B. J. Edwards, we believe, is due the credit of adding sodium hyposulphite to the mercury intensifier. This formula is as follows:—

No. 1.

Mercuric chloride (bichloride of mercury) ... ..	60 grains
Water ... ..	6 ounces

No. 2.

Potassium iodide ... ..	90 grains
Water ... ..	2 ounces

No. 3.

Sodium hyposulphite ... ..	120 grains
Water ... ..	2 ounces

The iodide solution is poured into the mercury solution, and then the solution of hyposulphite, which dissolves the iodide of mercury which has been formed.

The negative is fixed and washed, and the plate immersed in the above solution. Mr. Edwards says of it: "The intensifier acts very quickly, a few seconds being sufficient to give printing density to the thinnest negative. If required to work slower, add more hyposulphite, which will also alter and improve the colour of the negative. The shadows remain quite clear, there is no loss of detail, and the colour of the negative is all that can be desired. The negative must finally be well washed."

*Uranium Intensifier.*—Dr. Eder, in his "Modern Dry Plates," has recommended an uranium intensifier, which is made as follows:—

Uranium nitrate ... ..	15 grains
Potassium ferricyanide ... ..	15 "
Water... ..	4 ounces

Before using this, the plate must be thoroughly washed

(see page 209), as traces of hyposulphite cause a reduction of the uranic salt, and a consequent slight chocolate-coloured veil over the shadows. The plate is immersed in the solution, the details in the shadows are first attacked, and then the half-tones, and finally the high-lights. This intensification is permanent, and can be used with much advantage. Next to silver intensification we prefer this one, on account of its simplicity and permanency. Dr. Eder says that if a negative will not acquire sufficient intensity with uranium, it may be laid aside as useless, and with this we agree.

Varnished negatives may be intensified by removing the varnish first in warm methylated spirit, and, after rinsing under the tap, a tuft of cotton-wool should be applied to the surface. We think that there is but little more to be said regarding intensifying a negative. If it be weak and full of detail, we much prefer to make a thin transparency by contact, and from this another negative also by contact. By this means proper intensity can be given to the reproduced negative, which it is almost impossible to give to the original, so that all the rapidity of the gelatine plates is secured, together with the advantage of the collodion film for intensifying. We can strongly recommend this plan to our readers, as it has been most successful in our hands.

Another plan of getting intensity, which is said to be successful, was one recommended by Mr. Kennett, which is as follows :—

To 3 ounces of water add 1 ounce of sodium hyposulphite, to another 3 ounces add 1 ounce of ferrous sulphate (proto-sulphate of iron), mix, and allow them to stand a short time. When the plate has been well washed after development, it is placed in this mixture, and the image will be fixed and intensified to an intense black. A great advantage of this fixing solution is that the ferrous sulphate acts on the gelatine as a hardening solution, being even more astringent than alum.



*Fixing the Negatives.*—The formula for the hyposulphite fixing solution has been given at page 101, and need not be repeated. The strength there noted is perhaps rather great for many commercial plates, and it might be made up to about 1 ounce of hyposulphite to a half-pint of water. This reduces the chance of frilling. The use of cyanide is inadmissible, as it attacks the image (see page 211).

Before fixing the negative, it may be advisable to avoid all danger of frilling, and immerse it in an alum bath, which consists of a saturated solution of crystallized potash alum. The negative should be rinsed both before and after immersion. Five minutes in such a bath should be sufficient. The plate is next rinsed and placed in the fixing bath, and here it is that the use of iodide in the emulsion is disadvantageous. The hyposulphite attacks iodide much less rapidly than it does bromide; hence a plate prepared with iodide takes longer to fix.

After fixing the negative, it has to be thoroughly washed (unless it has to be intensified by Edwards' intensifier, see page 207). There are various contrivances for effecting this. A trough with vertical grooves to fit the plate is sometimes employed, which is a good plan where many negatives have to be washed, since the heavier saline solution sinks to the bottom of the water with which the trough is filled. Where only a few negatives are to be washed, flat dishes answer, about four changes of water being given, each change being made at the end of every half hour. To ensure thorough elimination of the hyposulphite, the plate may be subsequently immersed in the alum bath, and again washed. It must be recollected that thorough washing of any film depends on its thickness, and we may say that, as a rule, we consider six hours not too long washing for a thick film. When the plate is considered washed, if it is not to be intensified, it may be placed in a rack and allowed to dry spontaneously. If rapid drying be required, it may be flooded three

times with methylated spirit, when it will dry very readily, and can even be accelerated by a gentle heat.

*Varnishing the Negative.*—In order to prevent staining of the film by contact with silver paper during printing, a coating of varnish should be applied to the negative; but in order to avoid any chance of marking of the film, and before any varnish is applied, it is preferable that it should receive a coating of plain collodion. If it has received one to avoid frilling, it will be unnecessary to give it another. When the collodion is used, the writer's experience tells him that almost any varnish will answer. Enamel collodion is, perhaps, the best to employ; or it may be made by dissolving 6 grains of tough pyroxyline in half-ounce of ether and half-ounce of alcohol (820). The collodion is poured in a pool at the upper end of the dried plate, and flowed first to the right-hand top corner, next to the left-hand top corner, third to the left-hand bottom corner, and finally, as much as possible is drained off in the bottle at the bottom right-hand corner, giving the plate a gentle rocking motion in order to cause all lines to coalesce. The plate is then set up and allowed to dry. For a varnish, Mr. England uses seed lac in methylated spirit (a saturated solution), and then thinned down till it is of a proper consistency. The Autotype Company prepare a special varnish for gelatine plates, as does Mr. Hubbard one to use as a retouching medium. To apply the varnish, the plate should be gently warmed over a spirit-lamp or before the fire to such a heat that the back of the hand can only just bear the touch of the plate. The varnish is applied like the collodion. After draining of all excess, and rocking the plate, it is warmed till all spirit has evaporated and till the film is glossy. A lack of warmth will cause the film to dry "dead." Where many prints are not to be taken, it is believed that the film of collodion alone is a sufficient protection against the silver nitrate of the paper combining with the gelatine, and so causing a discolouration.

If a negative does get discoloured through this, a very dilute solution of potassium cyanide will usually clear away any marking that may have been made. But great care must be taken in using this solvent of the silver compound, as it attacks metallic silver when in such a state of fine division as that in which it is to be found in the gelatine plate.

## CHAPTER XLI.

### GELATINO-CHLORIDE EMULSION.

Dr. EDER and Captain Pizzighelli have recently worked out a most satisfactory gelatino-chloride emulsion, and, more important still, a satisfactory method of developing it when it is made. We have already alluded to it in Chapter XX. The formula they give is as follows :—

Sodium chloride	...	...	7½ grains
Gelatine, hard and soft (mixed)	25		„
Water	...	...	3½ dr.

This is emulsified by adding to it 15 grains of silver dissolved in 2 drachms of water. The silver may be precipitated and re-dissolved by ammonia, as given in Chapter XXXI., or it may be boiled and treated with ammonia, as given in the same chapter.

For our own part we prefer to use the boiling method, and to use the equivalent of sodium chloride for the ammonium bromide, omitting the iodide, as given in the standard formula in Chapter XXVII.

The formula thus stands :—

(2) Sodium chloride...	...	...	80 grains
(3) Nelson's No. 1 Gelatine	...	30	"
(4) Silver nitrate ...	...	200	"
(5) Nelson's No. 1 Gelatine	...	80	"
(6) Coignet's gold medal gela- tine, or Swiss gelatine }	...	80	"

To emulsify, we prefer the "reversed mode of mixing," using the quantities of water, &c., described on pages 141 and 142. The emulsion is boiled for half an hour, which changes the original canary-colour to blue-grey, a similar change to that effected in a bromide emulsion.

Development is effected by the ferrous-citro-oxalate developer, and also by hydrokinone (see page 238).

Dr. Eder's developer is given at page 237, and can be used with advantage, though it requires a rather prolonged exposure.

Contrary to the opinion of Dr. Eder, who places the maximum effect of the spectrum on silver chloride in the indigo about the line G, we have made it invariably at H, or near the visual limit of the violet end of the spectrum. It is for this reason that this emulsion is very much more rapid in the spring and summer and early autumn than in the winter and late autumn. We believe that on a bright summer's day (when the ultra-violet rays are abundant) it is as rapid as a good many bromide emulsions. If an emulsion containing silver iodide be made by omitting 10 grains of sodium chloride, and substituting for it  $3\frac{1}{2}$  grains of potassium iodide, an emulsion is made which can be developed with ferrous oxalate without any restrainer whatever, though, except for shortening the time of development, it has no advantage over the ferrous-citro-oxalate.

The development is carried out in a dish as usual.

Plates prepared with this emulsion should be carefully kept from the air, since they are apt to get tarnished, and

then develop badly. If they are wrapped in paper as described in the Appendix they may be kept an unlimited time.

We give an interesting table formed by Dr. Eder of the sensitiveness of silver chloride emulsion as compared with silver bromide in gelatine.

Sensitive Substances.	Necessary time of exposure to bring about a vigorous image.	Sensitive-ness of the combinations.
AgBr developed with ferrous oxalate or alkaline pyrogallic ... ..	1	100
AgBr, with acid pyrogallic acid, ferrous sulphate, and silver nitrate ... ..	5-7	16-20
AgI ditto ... ditto ... ..	4-5	20-25
AgCl with alkaline pyrogallic... ..	6-8	13-17
AgCl with ferro-citrate and a trace of hyposulphite ...	10	10
AgCl with ferro-citrate alone ... ..	50	2
AgCl with pyrogallic acid alone ... ..	100	1
AgCl with hydrokinone and ammonium-carbonate ...	150	0.7
AgCl with hæmatoxylin and ammonium-carbonate ...	500	0.2
AgCl without development, commenceemnt of blackening... ..	150-200	.05-.07



## CHAPTER XLII.

### GELATINIZED PAPERS.

**T**H**ERE** are in the market at the present time two or three gelatinized papers containing silver bromide, and it is to be presumed that these papers are prepared with gelatine emulsion. At first sight, nothing would appear simpler than to coat paper with an emulsion, but we may at once say that it is not by any means so simple as it seems. We will endeavour to give a description, however, of a plan by which it can be accomplished in a satisfactory manner. Firstly, the emulsion may be gelatino-bromide, gelatino-bromo-iodide, or gelatino-chloride, and may be prepared by any of the methods given in the previous chapters. It may be boiled or not boiled, according as great or little sensitiveness is required. For our own part, we like a paper which is only moderately sensitive, since there is no great need to take extremely rapid pictures. One thing, however, we may remark, that with bromo-iodide and bromide emulsions the colour resulting from a boiled emulsion has a tendency to be less green than one prepared without boiling. This remark also applies to gelatino-chloride emulsion, but with not such force.

The amount of water with which the finished emulsion is made will be found to be about correct; but the operator must, by an experiment with an emulsion, judge whether

the gelatine he uses should be increased or diminished. A hard gelatine, for instance, may allow dilution with water. A golden principle to remember is, however, that the thicker you require your film, the less water there should be with the gelatine. If a film is wanted as thick as that for carbon printing, it can be obtained by using 100 grains of gelatine to each ounce of water, instead of about as much to 4 ounces of water. If a thick film, however, be required, we recommend that the operations we are going to describe be repeated twice—or even three times.

The paper to be coated may be medium Saxe paper, or paper of that description, with not too high a glaze on it. It should be cut up into the sized sheets required, and carefully dusted from every particle of dust. The emulsion should be heated, and placed in a shallow dish somewhat larger than the sheet to be coated, and the fluid should be a quarter of an inch in depth. The dish must be kept warm by placing it on a closed shallow tin box containing water heated by a spirit lamp beneath, or some other similar means. When heated to about 130° F. (the temperature depending upon the kind of gelatine employed), the paper is turned up for about a quarter of an inch at one end, and the sheet coiled up in a roll, the coil being made towards the turned-up end. The turned-up end is placed on the emulsion, and the coil gradually allowed to unroll itself till the whole surface except the turned-up end rests upon the emulsion. After resting a minute the end is seized by two hands, and a glass plate having been made to rest on the dish, the uncoated side of the paper is drawn on to the plate, where it remains till it is set,\* when it is hung up by clips to dry in a cupboard or other place free from dust. The paper thus prepared should present an even film, free from all "ridges" or "tear-markings," and, when developed, should present a vigorous image by transmitted

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\* It is a good precaution to take to place a muslin-covered frame over the glass holding the gelatinized paper to protect it from dust.

light. To develop a bromide or bromo-iodide emulsion we recommend a ferrous oxalate developer, using to every ounce employed about 10 drops of a 20-grain solution of potassium bromide. This gives a blacker image than the ferrous oxalate alone. The Photographic Artists' Co-operative Supply Association, who issue paper as above, recommend the following form of ferrous-oxalate :—

*Stock Solutions.*

1.—Chrome alum ... ..	100 grains
Boiling water ... ..	5 ounces
2.—Oxalic acid ... ..	30 grains
Water ... ..	5 ounces
A.—Potassium oxalate ... ..	4 ounces
Glycerine ... ..	$\frac{1}{2}$ ounce
Chrome-alum solution (No. 1) ... ..	$\frac{1}{2}$ "
Oxalic-acid solution (No. 2)... ..	$\frac{1}{2}$ "
Water ... ..	15 ounces
B.—Ferrous sulphate ... ..	4 ounces
Sulphuric acid ... ..	10 minims
Water ... ..	16 ounces

To develop, 8 parts of A are mixed with 1 part of B.

An excellent developer may be made by mixing equal portions of the ordinary oxalate developer (see Appendix) and the above. For fixing—

Sodium hyposulphite ... ..	4 ounces
Water ... ..	20 "

They further recommend the following for bleaching if necessary :—

A saturated solution of borax or	
sulphuric acid ... ..	1 ounce
Water ... ..	100 ounces

And to harden the film, common alum (a saturated solution), or chrome alum of a strength 20 grains to each ounce of water.

For a charming black tone we recommend that boiled chloride emulsion be used. It is very easily prepared, and presents great facility of development with the ferrous-citro-oxalate developer given in the Appendix. The bromide and bromo-iodide papers may also be developed with the usual alkaline developer, using citric acid to keep the solutions from discolouring. The addition of sodium sulphite, as recommended by Mr. Berkeley, will answer the same purpose. The fixing bath should be the same as above. When the washing is complete, which will take two or three hours, the prints may be toned if required. A beautiful brown-black tone is given by a weak solution of ammonium sulphide, the colour being permanent. All excess should, of course, be well washed out. A solution of sulphuretted hydrogen in water will answer the same purpose. Against the use of such solutions we are aware that many photographers will, metaphorically, hold up their hands, as they will remember the dread they have of bringing any sulphur compounds in contact with a print on albumenized paper. They should recollect, however, that the conditions are totally different. It is the organic compound of silver which gives rise to fading, and *not* the sulphuration of the metallic silver. Sulphide of silver is about as permanent a silver compound as can exist, and there can be no danger of its fading. Great care must be taken to eliminate all traces of iron salts by washing after development, when using the above solutions, otherwise the white will be dirty. This dirty green appearance, however, may be got rid of by passing the print through dilute hydrochloric acid. The tone assumed by the prints with this treatment is a warm brown black, reaching a jet black if prolonged.

An improvement in the tone may also be given by using the uranium intensifier (see page 207). Resort may also be had to gold and platinum toning; but the above will give almost every variety. If paper be given a coating of india-rubber solution, or gelatine, and then a

coating of normal collodion (10 grains of pyroxyline to 1 ounce of ether and 1 ounce of alcohol), the paper may be coated by turning up the edges to form it into a little dish, and holding it on a glass plate. The emulsion is then allowed to set, and eventually hung up to dry. .

In both methods of preparing the paper the desiccation takes place much more rapidly than with a gelatine plate, since there are two surfaces by which the drying effect of the air is utilized.

For direct enlarged positives, the thinly-coated paper is extremely useful, an optical lantern can be used, and good prints secured with but very short exposure. As an example of the exposure necessary for this, we have produced an enlargement of six diameters by an exposure of three minutes when using a triple-wick oil lamp as the source of illumination. It also should take the place of collodion transfers for working upon in oils or crayons.

## CHAPTER XLIII.

### ACETO-GELATINE EMULSIONS.

DR. H. W. VOGEL experimented in production of emulsions which should combine the rapidity of the ordinary gelatine plate with the ease of coating of a collodion emulsion. His emulsions are made as follows, according to the English specification of his patent. He rightly claims for himself the novelty of being able to mix a solution of pyroxyline with one of gelatine, and thus getting the advantages of both emulsions. Any gelatine emulsion (such as that described, for instance, in Chap. XXVII.) is prepared as usual, and the pellicle dried. This dried emulsion is then dissolved in one of the fatty acids (such as formic acetic, or propionic; acetic acid, however, by preference, on account of its cheapness). To effect this it is warmed in the acid, using three to ten times as much acid as pellicle. The quantity of acid depends on the kind of gelatine originally employed. Sufficient alcohol is now added to this, till it is of proper consistency for flowing over the plate when heated to a temperature of about 90° F. When cold the emulsion sets in a gelatinous mass. Plates may be coated with this emulsion *per se*: the emulsion is flowed over like collodion, and any excess drained into the bottle. In very hot weather, however, it is better to lay the plates flat for a short time, since sufficient emul-



sion is difficult to retain on the plate if thoroughly drained. In order to give tenacity, Dr. Vogel, as before stated, mixes pyroxyline with his emulsion.

His formula is this :—

Pyroxyline	...	...	...	20 grains
Acetic acid	...	...	...	1 ounce
Alcohol...	...	...	...	1 „

This form of collodion is mixed with equal quantities of the gelatine emulsion just described. The plates formed by this collodio-gelatine emulsion can be used wet or dry. Another method Dr. Vogel describes, which is as follows. Collodion emulsion is prepared in the ordinary way (see page 45), and dried; 70 grains of the pellicle are dissolved in 3 ounces of alcohol, and  $1\frac{3}{4}$  ounce of acetic acid. 20 grains of gelatine are dissolved in  $3\frac{1}{2}$  drachms of acetic acid, and added to it. Plates are coated in the ordinary manner by it.

A plan which we adopted before the publication of the formula was to take gelatine pellicle (say 50 grains), dissolve by aid of the heat of hot water in the smallest quantity of acetic acid, adding drop by drop till the solution is perfect. Methylated spirit was added till it flowed nicely over a trial plate, when it was filtered through cotton wool, washed, and was then ready for use. The plates must have a very adhesive substratum; that given at page 184 is effective, whilst another is [india-rubber in solution made by dissolving india-rubber paste in benzole till it has the consistency of cream. There is a tendency, however, with the latter for the film to crack, with the former none whatever.

The drawback to this process is the smell of the acetic acid, which is decidedly objectionable. Again, too, it is of necessity a more expensive process, since the solvents of the gelatine are not as common as tap water. On the other hand, the negatives obtained by it are excellent; the gelatine is apparently changed in quality, and allows

the developer to permeate easily, and consequently great density is obtained. The sensitiveness of the emulsion is slightly diminished according to our experience, but there is a perfect immunity from spots of any description. There is one great convenience in this emulsion, which is, that it can be kept in a bottle corked, and used for coating plates as required, instead of having to coat more plates than sometimes may be convenient. Care must be taken, in coating the plates, that the emulsion does not run into ribs. The plates should be rocked as with collodion emulsion, and then there is no danger of this defect.

For developing, Dr. Vogel recommends the following as giving the best results :—

- 1.—Sodium, mono-carbonate  
     (crystalline) ... 200 grains  
     Potassium bromide...  $1\frac{1}{2}$  to 2 „  
     Water ...  $\frac{3}{4}$  ounce
- 2.—Pyrogallie acid ... 50 grains  
     Alcohol ... 1 ounce

3.—Four parts of No. 1 are mixed with one part of No. 2 for a normal exposure. The development must be modified according to circumstances (see page 192).

Dr. Vogel also uses Nelson's developer (page 198), and the ferrous oxalate (page 235). In regard to this latter he uses it in a somewhat different form to that given. His formula is as follows :—

- 1.—Potassium oxalate (neutral) ... 10 ounces  
     Water ... 30 „
- 2.—Potassium bromide ... 12 grains  
     Water ...  $\frac{1}{4}$  ounce
- 3.—Hyposulphite of soda ... 2 grains  
     Water ... 1 ounce
- 4.—Ferrous sulphate ... 1 ounce  
     Water ... 3 ounces

To develop, he mixed

No. I	...	...	...	1½ ounce
No. II	...	...	...	15 drops
No. III*	...	...	...	15 „

When well mixed, he adds ½-ounce of No. 4, and again mixes and applies to plates.

M. Konarzewski also gives a formula for a collodio-gelatine emulsion :—

Alcohol 805	...	...	...	2 ounces
Glacial acetic acid	...	...	...	2 „
Pyroxyline	...	...	...	18 grains

To this collodion 180 grains of gelatine emulsion are added, and dissolved by aid of heating in hot water. He recommends a substratum of albumen and silicate of soda (page 184).

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\* If the plates be hard, he uses 30 drops of No. III. instead of 15.

## CHAPTER XLIV.

### DEFECTS IN GELATINE PLATES.

*Frilling.*—What is meant by frilling is the gelatine film leaving the glass plate in folds or wrinkles, and a greater nuisance than this cannot be met with. It is generally met with when fixing the plate, though we have sometimes met with it during the development, especially in hot weather. We will endeavour to state the causes of frilling as they are known. Frilling is often caused by the use of unsuitable gelatine, possessing but little tenacity. The more the qualities of gelatine are like glue the less chance there is of meeting with this vexatious evil. If gelatine, however, were like glue in respect to hardness, the difficulty of developing a plate would be very great, since it is too hard. To meet this objection, a certain proportion of a less tenacious gelatine is mixed with the harder kind, a very good index of the tenacity being the temperature at which it melts after swelling. The addition of chrome alum to an emulsion also prevents it to a great extent. The objections to chrome alum are that it increases the tenacity of the gelatine, and prevents easy development; hence it should be used sparingly.

Gelatine that has been cooked for a long time has a special tendency to frill, and, unless fresh gelatine be

added to the emulsion, in some cases the frilling is inevitable. Long cooking (in warm weather particularly) means decomposition of the gelatine, and decomposed gelatine is very detrimental in preparing a dry plate. Boiling for a short time has much the same effect on the gelatine as cooking at a lower temperature; hence, to avoid frilling, it is better on the whole not to boil the emulsion with the full amount of gelatine.

Another source of frilling is the plate being improperly cleaned. If water will not flow in a uniform sheet from a plate, it may be well understood that there will be but little adhesion between it and an aqueous solution of gelatine (see page 182). This we believe to be one fruitful source of the evil.

Another source of frilling is unequal drying. Thus, if plates be dried in an unventilated box, it will usually be found that a central patch refuses to dry till long after the outsides are completely desiccated. At the junction of this central patch with the neighbouring gelatine frilling is to be looked for. It will spread to the parts which have been the longest in drying. This is due to a false tension set up in the film, and can only be conquered by drying the plate by means of alcohol, or by using a proper drying cupboard.

Again, when plates are coated in hot weather, unless precautions as innumeraled in Chap. XXXIII. are taken, they take long to set. The emulsion remains liquid on the plate for sufficient time to allow the heavier particles of silver bromide\* to settle down on the surface of the glass. This of course diminishes the surface to which adhesion can take place. We believe that most of the frilling which takes place in plates prepared in hot weather may be traced to this cause. When washing after fixing, frilling is often caused by allowing a stream of water from the

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\* This is particularly liable to happen when the emulsion has been long boiled or carelessly mixed.

tap to impinge on the plate. This should never be allowed if the film is at all delicate.

At page 147 it has already been stated that chrome alum is used with a gelatine emulsion. This is recommended to prevent frilling when soft gelatine is used in hot weather. Plates which frill or blister will not show any signs of so doing if kept for a few months.

A general remedy for frilling is to coat the plate with normal collodion containing about six grains of tough pyroxyline to the ounce of solvents. The formula would be thus:—

Tough pyroxyline	...	...	6 grains
Alcohol (.820)	...	...	$\frac{1}{2}$ ounce
Ether (.725)	...	...	$\frac{1}{2}$ „

This may be applied to the film immediately before developing the plate; the solvents are washed away in a dish of clean water first, and, when all repellent action is gone, the developing solutions applied. If the film has been allowed to dry, a solution of one part of ether to three of alcohol will render it pervious to the developing solutions.\* In some batches of plates frilling is so obstinate that, although collodion be applied, the film has a tendency to curl off from the edges of the plate. It is advisable, when such is suspected, to run a brush with an india-rubber solution round the edges, to prevent the water having access to that part of the film. When fixing such plates it not unfrequently happens that blisters appear, and, if allowed to remain as they were, will spoil the negative. To avoid this, we wash the plate under the tap till all the blisters join, and the film presents the appearance of a sack containing water. A prick at one corner of the plate lets this liquid free, and the washing can take place as usual. The obstinate cases of frilling usually occur through plates being prepared in very hot

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\* We have found this essential in intensifying negatives which have been treated with collodion after fixing and drying.



weather, and the film being dried without first setting. Another palliative is, in development, to use a mixture of half alcohol and half water, in which to dissolve the pyrogalllic acid, using twice the amount to each ounce to that usually employed. This extra pyrogalllic acid is required, as the developer turns black sooner in consequence of using the alcohol. If this stops frilling during development, but frilling takes place during fixing, the plate should next be immersed in a strong alum bath (see page 209) for a few seconds, be very carefully rinsed with water, and then set up to dry. When once dry, it may be fixed without any risk. A more expensive method is to add to the hyposulphite bath as much methylated spirit as it will bear without precipitating the salt.

Some writers state that, by immersing the plate in a saturated solution of Epsom salts, frilling is avoided: we have not succeeded ourselves in proving its universal efficacy.

*Blisters on the Film.*—Blisters on a film are the usual preliminaries to frilling. When they commence, further damage may usually be avoided by flooding the plate with methylated spirit. This extracts the water, and with it any soluble salt that may be left, and the plate speedily dries, which is an advantage if it be fixed. Blisters are usually found to follow the rubbing marks of the polishing cloth, if such be used. The cure here is self-evident. They also are to be found in places between which the film has dried quickly and slowly.

*Red Fog.*—The writer fortunately knows very little about this disaster, but it is found to occur if the silver nitrate is in excess of the salts with which it should combine. Cyanide will sometimes eliminate it from a film, but this remedy must be used with caution.

*Green Fog.*—This fog is due to decomposed gelatine and oxidized pyrogalllic acid. Green by reflected light, it is pink by transmitted light, being dichroic. This at once points to the fact that this fog is somewhat of the

nature of a dye, and every oxidizing agent ought to destroy it. In some cases we have immersed the film in a strong solution of bichromate of potash, and on afterwards washing, the fog has disappeared; but whether it is a certain cure, we hesitate to say; it is, at any rate, worth trying.

*General Fog.*—By general fog we mean the fog produced during development, and is caused by the partial reduction of the silver salt all over the film. This is probably due to the decomposition of the gelatine by long cooking, the products of which in the presence of a developer are apt to react on the silver salt, and produce a partial reduction in it. The production of this kind of fog, and electrical disturbance in the atmosphere, are apt to go together. In unfavourable weather, a few drops of a saturated solution of salycic acid should be added to the gelatine during boiling or prolonged emulsification; this will generally check or entirely prevent the decomposition. An excess of silver is likewise very likely to produce the evil, but the presence of iodide in the emulsion will almost certainly cure it. Another fruitful source of fog is the light admitted to the plates during preparation or development. The light should be tested by putting a plate in the dark slide, and drawing up half the front, and exposing the half-plate to the light for ten minutes. If the fog be due to this cause, the plate on development is sure to show it by an increased reduction of metallic silver in the part so exposed.

Whatever may be the cause of fog—whether the emulsion itself be in fault, or whether the plates have seen light—we have found that, as in the collodio-bromide process, there is one certain sure cure. If the emulsion be at fault, squeeze it into water (see page 25) containing 10 grains of potassium bichromate to each ounce, and allow it to rest for an hour, and then wash again for a couple of hours more. If all the bichromate be not taken out by this washing, it is not of much consequence, since

when dry it is inactive. The sensitiveness after this treatment is not much diminished, and the negatives taken with it are beautifully bright. Plates may be treated in precisely the same manner, and give unveiled pictures. There is a *slight* diminution of sensitiveness if the bichromate be not at all washed out, but nothing to hurt except where very great rapidity is required.

Another cure is the addition of a few grains of cupric chloride. This diminishes the sensitiveness slightly, but is most effectual, the negatives yielding bright and brilliant images. A remarkable fact about the addition of the cupric chloride is, that the grey form of bromide is converted into the red form if much of the copper salt be employed. The addition of a few grains of ferricyanide of potassium with a little bromide of potassium (see page 13) is also a perfect cure, but this slows the emulsion.

Another method is to add a few drops of hydrochloric acid to the emulsion, or to slightly acidify the first wash water with it; about 1 drachm to a pint of water is generally ample. The length of time which the emulsion should be in contact with the acidified water depends on the size of the mesh of the canvas through which the emulsion is squeezed. For a medium size, half an hour suffices. The emulsion has a tendency to become insoluble by this method.

*Flatness of Image* is usually due to over-exposure and development with the alkaline developer: the use of ferrous oxalate mitigates the evil, whilst if iodide be in the film, we have never found any great lack of density to arise. Feebleness of the image is also often caused by too thin a coating of emulsion. In our own experience, a thick film is a desideratum, giving all the necessary density to the image with facility. Remember that when a vigorous image is required, it is most readily obtained by using a *freshly prepared* and strong ferrous oxalate solution (see page 235).

*Too great Density of Image* is sometimes met with, and

can be remedied by applying ferric chloride to the film, and then subsequently immersing in the hyposulphite of soda fixing bath.

The formula recommended is—

Ferric chloride...	...	...	1 drachm
Water ...	...	...	4 ounces.

This is flowed over the plate a short time, and then, after washing, the plate is immersed in the fixing bath. The solution acts very vigorously, and should be diluted if only a small reduction is required. Local reduction may be effected by using a paint brush charged with this solution on the moistened film. This practice is not, however, much to be commended, as it is rather working in the dark.

Density may also be diminished by the use of a strong solution of cyanide. Local reduction may be given by moistening the parts required to be reduced with water by a paint brush, and then applying the cyanide in the same manner. The reduction can be seen progressing.

There are a variety of formulæ extant for reducing negatives. Perhaps the best is eau de javelle, which can be obtained of all chemists, but which is made as follows:

Dry chloride of lime	...	...	2 ounces
Carbonate of potash	...	...	4 „
Water	...	...	40 „

The lime is mixed with 30 ounces of the water, and the carbonate dissolved in the other 10 ounces. The solutions are mixed, boiled, and filtered. The filtered solution should be diluted, and the plate immersed in it till reduction takes place. The plate should be fixed, and again washed.

*Yellow Stains.*—Usually a yellowish veil appears to dim the brightness of the shadows when the development has been effected by the alkaline developer. This may be removed, if thought requisite, by the application of one or two drops of hydrochloric acid to an ounce of

water, and floating it over the surface of the plate. The film must be washed almost immediately, as the acid is apt to cause frilling.

Another formula, due to Mr. J. Cowell, is to immerse the plate in—

Alum	...	...	...	2 ounces
Citric acid	...	...	...	1 ounce
Water	...	...	...	10 ounces.

Another formula is—

Saturated solution of alum	...	20 ounces
Hydrochloric acid	...	$\frac{1}{2}$ ounce

The negative should be well washed in all cases after the application of either of them.

*Too Granular an Emulsion* is usually due to bad mixing of the soluble bromide and the silver nitrate, but it may also be caused by over-boiling, and also by too small a quantity of gelatine in the boiling operation. Digesting too long with ammonia, as in Van Monckhoven's process, has the same effect. There is no cure for this evil.

*Opaque Spots* on a plate are almost invariably due to dust settling on the film when drying; they also may be due to imperfect filtering of the emulsion.

*Semi-transparent Spots* on the plate before development are generally due to (1st) excrescences on the glass plate, or (2nd) to the use of gelatine containing grease.

As has already been pointed out on page 135, certain gelatines are apt to contain grease, and that so intimately that soaking in ether or washing with ammonia will not eliminate it. A specific is as follows:—We will suppose that 80 grains of Coignet's gelatine are required: 90 grains are weighed out, soaked in water, drained, and melted. The liquid is then very slowly poured, almost drop by drop, into methylated spirit, free from resin, where it is precipitated in shreds of a white pasty character; after it is all precipitated the spirit is poured



off, and a slight rinse with fresh spirit given, and then it is covered with water, in which it should remain till the whiteness disappears. The water should then be changed, and the gelatine drained and redissolved; about 10 grains out of the 90 seem to be dissolved in the mixture of alcohol and water. Emulsions made with this gelatine will be markedly free from grease spots. The same method may be adopted for large quantities of gelatine, omitting the final wash with water, and leaving it to dry spontaneously. This is best done on glazed dishes. The gelatine can be broken up, weighed, and used in the usual manner.

*Dull Spots on the Negative* are also due to the use of gelatine which contains greasy matter.

*Want of Density* in a negative may be caused by over-exposure (see page 229), but it more often arises from the emulsion itself. A rapid emulsion will always give a feebler image than a slow emulsion, although to form the image the same amount of silver may be reduced. This shows that the silver is in such a state of aggregation that it does not possess what may be called covering powers. We have found that the addition of a chloride emulsion materially aids the production of density. If one-fifth part of an emulsion prepared according to Chapter XLI. be added to an emulsion lacking in density-giving qualities, it will be secured without detriment to the sensitiveness. The range of sensitiveness will be slightly altered (see page 241). A hard gelatine is also conducive to feeble images. If prepared plates give feeble images, resort must be had to intensifying.



## APPENDIX.

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A *Liebig's Condenser* is a very useful piece of apparatus for rectifying alcohol and distilling emulsion, but it requires certain precautions to be taken to ensure safety. The apparatus arranged as in fig. 16 is suitable for the purpose.

The condenser consists of two parts: first, a straight glass tube (*b*), bent at the ends, to which the flask is attached; the second, a jacket (*c*) surrounding the bulk of the tube as shown in the figure. The jacket has two

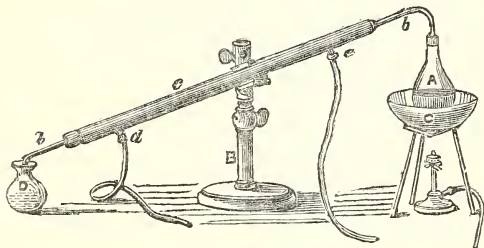


Fig. 16.

short tubes (*d* and *e*) connected with it, *d* being that through which the cold water is supplied to the jacket, and *e* that through which the warm water is forced out. A couple of india-rubber corks are bored to fit the central

tube and to close the ends of the larger tubes. The condenser can be held by a clamp, B. The cold water can be supplied from a water tap, a pinch-cock being used on the india-rubber tube from *d*, so as to allow a very small flow; or it may be supplied from a jar with a syphon arrangement, if care be taken to keep the bottom of the vessel above the highest end of the jacket. For distilling alcohol or an emulsion, the flask should be held in a metal bowl, C, filled with water, but the bottom of the flask should not touch the bottom of the bowl, otherwise there is danger of bumping and fracture of the former. In practice, we have found that the ring formed by blotting-paper is sufficient protection to the flask. This is placed in the bowl, and the flask placed upon it. A jacket may surround the source of heat, which may be a spirit-lamp, a gas jet, or an oil lamp, but is unnecessary when there is no draught in the place where the distillation is being carried on. The alcohol distils over, and is condensed in the tube *b*, and drops into the flask D. It is not absolutely necessary that the flask should not come in contact with the flame of the source of heat, but it is safer not to allow it to do so.

If we have alcohol of (say)  $\cdot 830$  specific gravity (a very common one, by-the-bye) and we wish to rectify it, the best method is to place in the bottle containing it sufficient freshly burnt unslaked lime to completely saturate the spirit, leaving, in fact, very little liquid above the sediment; after standing two or three days this mass must be put in retort, and the distillation proceeded with. The distilled spirit will be found to be of a specific gravity of  $\cdot 795$ . An anhydrous spirit of this specific gravity is very useful to have in stock, as it enables water to be used in the operations of making emulsions without exposing the film to the evil of crappiness. The spirit may be distilled till the lime appears quite dry, for the latter will hold the water in combination at a temperature far beyond the boiling point of water.

If spirit be distilled from alcohol containing about half as much lime as indicated above, it will be found that the specific gravity of the distillate will be about .812, which is a very convenient mixture of alcohol and water.

### ORGANIC IRON DEVELOPERS.

*Simple form of Ferrous-oxalate Developer.*—A saturated solution of the neutral potassium oxalate is first prepared. A crystal of oxalic acid is next added, to prevent the slightest trace of alkalinity. At one time we used to add ferrous oxalate to a boiling potassium oxalate solution, only so much of the oxalate being added as to leave a slight portion of the ferrous compound undissolved. We prefer now to add the ferrous oxalate to the cold saturated solution of the potassium salt, and to allow them to remain in contact with one another for twenty-four hours, shaking occasionally. The clear solution can be decanted off. This method prevents the deposition of crystals on the sides of the bottles, which always are deposited if the ferrous oxalate be heated with the potassium oxalate. The solution will be of a deep red colour.

The ferrous oxalate solution rapidly oxidizes by contact with the air, as already hinted at, and our own practice is to fill 4-ounce bottles with it, cork them up, and then to lute the corks with solid paraffin. Mr. Warnerke has a still better plan. He uses a stoppered bottle having an opening near the bottom, such as can be procured at any chemical dealer's. Into this opening he fits a cork carrying a small glass tube; on to the end of this (outside the bottle, of course) he fits a piece of india-rubber tubing, and connects this with a similar piece of bent glass tubing, which reaches nearly as high as the top of the bottle. He fills the bottle two-thirds way up with the ferrous oxalate solution, and then pours in a layer of liquid paraffin. This prevents any access of air to the

solution. To get at the solution, the bent tube is turned down below the level of the paraffin, and the developing cup or bottle filled.

*Dr. Eder's Ferrous Oxalate.*—Mr. York, working on the directions of Dr. Eder, gives the following formula:—

No. 1.

Ferrous sulphate	...	...	160 grains
Water ...	...	...	1 ounce

No. 2.

Potassium oxalate (neutral)	...	...	1 ounce
Water ...	...	...	3 ounces

This makes up 4 ounces of developer, and by using these quantities, saturated solutions are obtained. Personally, we prefer 4 parts of No. 1 to 1 of No. 1.

*Strong Ferrous Oxalate Developer prepared with Ferrous Sulphate.*—A still stronger form of ferrous oxalate developer can be made by taking a saturated solution of potassium oxalate and adding to it *crystals* of ferrous sulphate. These must be added cautiously, since part of the potassium oxalate is converted into ferrous oxalate, and the remainder holds it in solution.

Mr. York's formula for the potassium oxalate may be taken, and to it 200 grains of sulphate of iron be added (powdered up in a mortar by preference). It will probably be found that some of the yellow oxalate will precipitate, in which case *crystals* of potassium oxalate must be added to the solution till such precipitate is redissolved.

*Ferrous Citrate Developer.*—The following is the method of making ferrous citrate developer according to Dr. Eder and Capt. Pizzighelli's plan:—600 grains of citric acid are dissolved in  $4\frac{1}{2}$  ounces of water with the aid of heat, and exactly neutralized with ammonia; 400 grains of citric acid are then added, and the bulk of the fluid made up to 9 ounces of water; 3 drachms of this solution

are mixed with 1 drachm of a saturated solution of ferrous sulphate and 12 minims of a solution of sodium chloride (30 grains to the ounce of water).

Ferrous citrate may be purchased and dissolved in a saturated solution of ammonium citrate, adding citric acid if required to give a clear picture.

*Ferrous-Citro-Oxalate.*—This developer, introduced by the writer, is made as follows:—

Potassium citrate (neutral)	...	100 grains
Ferrous oxalate	... ..	22 „
Water	... ..	1 ounce

The potassium citrate is first dissolved in a flask by heat, and, when nearly boiling, the ferrous oxalate is added, and shaken up in it, a cork being used to prevent the access of air to it. This quantity of ferrous-oxalate should just dissolve. It may be cooled by allowing cold water to flow over it, and should then have a citrony-red colour.

A weaker solution is made the same way with the following formula:—

Potassium citrate	... ..	50 grains
Ferrous oxalate	... ..	12 „
Water	... ..	1 ounce

These solutions keep well when corked up in bottles. There is no deposit from keeping even when oxidized, which is shown by the solution turning an olive green colour.

*Hydrokinone Developer.*—This developer being expensive at the present time, it is merely placed in this work for reference. It has a slightly greater developing power than pyrogallic acid. To make a normal developer—

#### No. 1.

Hydrokinone	... ..	6 to 12 grains
Water	... ..	1 ounce.

#### No. 2.

Carbonate of ammonia in water ... A saturated solution.  
To every ounce of No. 1 use 1 drachm of No. 2.

*On Intensifying Gelatine Negatives with Silver before Fixing.*—The great danger in intensifying gelatine plates after fixing are red stains, and this has usually been attributed to the fact that hyposulphite is left in the film. In Chapter XL. it has been shown how this salt can be decomposed, but with some the same stains occur, even when it is so altered. The same may be said when intensifying gelatine plates before fixing, when no hyposulphite has been used. After some experimentation, the writer has been forced to the conclusion that certain gelatines, when boiled, decompose into some compound which is liable to combine readily with silver, and that it is this body which, in reality, is often the cause of the stains. Plates prepared with an emulsion which has not been boiled can usually be intensified both before and after (when all the hyposulphite has been eliminated) fixing without any staining whatever. In the case of these films the former condition is the better in which to give intensity. The plan to adopt when using boiled emulsions is to immerse the plate in alum (or chrome alum), rinse, and dry thoroughly, and then intensify. By this procedure the film is not penetrated by the intensifying solutions, and consequently any stain, if there be any, is a surface stain, which can be immediately eliminated by a weak solution of cyanide.

*Intensifying Solutions.*—The following is a good standard intensifier for both collodion and gelatine plates :—

No. 1.

Pyrogallie acid	...	...	2 grains
Citric acid	...	...	2 „
Water ...	...	...	1 ounce.

No. 2.

Silver nitrate	...	...	20 grains
Water ...	...	...	1 ounce.

To intensify, to every ounce of No. 1, 20 drops of No. 2



should be added. It is well to flow No. 1 over the plate first, and then to drop No. 2 into the cup and return No. 1 on to it. The solution gradually gets a dark colour; but as long as it is perfectly clear it may be used with impunity. Directly a precipitation of metallic silver is observed, fresh solution should be mixed.

*Slow Collodion Emulsion Process for Transparencies.*—The following formula has met with approval for the preparation of a collodion emulsion for transparencies, and was one which we used for producing intense negatives: 50 grains of silver nitrate are dissolved in  $\frac{1}{2}$  drachm of water, and  $\frac{1}{2}$  ounce of boiling alcohol (.805) added. This is poured on 10 grains of pyroxyline, and then 1 ounce of ether added to dissolve the cotton. The silver very probably will precipitate in very fine grains, but this is of no consequence. In another  $\frac{1}{2}$  ounce of alcohol, 40 grains of zinc bromide are dissolved, and this solution is gradually added to the above collodion with shaking. Such an emulsion will be found perfectly free from mottling caused by excess of water, and will flow smoothly. When a plate is coated, it is washed, and any preservative used (preferably beer), to which to every  $\frac{1}{2}$  pint a lump of sugar of the size of a large hazel nut is added.

*Slow Gelatine Emulsion.*—Slow gelatine emulsion may be prepared by the formula given in Chap. XXXVII., by reducing the time of boiling to five minutes. If emulsification, as described in Chap. XXXVI., be accepted, it will be found that after twelve hours it will be in a condition to give a slow plate. Any emulsion may be made slow by adding 10 grains of copper chloride to it after boiling. These slow plates give wonderful density.

*Backing for Gelatine Plates.*—It will be found that, with most gelatine plates, blurring is a very frequent occurrence if the exposure be at all prolonged. This blurring can be nearly got rid of by the use of a backing in optical contact with the back of the plate. The amount of blurring that may be expected can be judged by placing

the film side of the plate against printed matter, and seeing with what degree of distinctness it can be read.

At page 84 a formula for backing collodion plates was given, but for gelatine plates it is as well to have some material which is soluble in alcohol rather than in water, for very evident reasons. There is nothing better than asphaltum dissolved in benzine, and this remains intact during development, and can be removed with a little turpentine or benzine afterwards. Another plan is to dissolve aurine in collodion, and coat the back of the plate with this. Water will readily remove the film.

*Recovery of Residues.*—The residues from gelatine emulsions may be recovered by two methods. First, by adding 1-10th part of its bulk of a saturated solution of caustic potash or soda, and then boiling. This precipitates the silver in the metallic state, and kills the viscosity of the gelatine. The solution eventually becomes colourless, and the black deposit left contains all the metallic silver. This may be dried, burnt slightly at a red heat, and treated with nitric acid, and fresh silver nitrate procured; or it may be added direct to the other residues (old films, whether of collodion or gelatine, may be similarly treated).

The second method is to add half an ounce of hydrochloric or sulphuric acid to each ten ounces of emulsion, and to boil. The acid destroys the gelatine, and the silver bromide and iodide precipitate at the bottom of the glazed saucepan or vessel in which it may have been boiled. After decanting the supernatant fluid, the precipitate is added to the residues for reduction.

*Coloured Medium for Windows.*—Mr. Warnerke has adopted an admirable material for colouring windows. It is simply the ruby-coloured cloth used by bookbinders. When examined by the spectroscope, two thicknesses are found to do away with every trace of blue, leaving behind merely a band of red. The price is ridiculously

low compared with most materials used, and we can recommend it to our readers.

*Effect of Mixtures of the Haloids.*—Since the earlier parts of this book were put in type, the writer has made a series of investigations into the effect of mixtures of iodide and bromide, iodide and chloride, bromide and chloride, and all these haloid silver salts. As a result, he finds that when mixtures of iodide and bromide or iodide and chloride are used, that a secondary action is set up by the liberation of the iodine, chlorine, and bromine, and that a new molecule is formed which is a true double salt. This double salt is more sensitive to the blue than it is to the violet; hence, by using a large part of iodide (say  $\frac{1}{4}$ ) with bromide, it is possible to make emulsions which shall, we believe, render landscapes better than the ordinary bromide alone. The addition of a small quantity of iodide is at all times advisable on this account. For further particulars of this investigation, the reader is referred to the Proceedings of the Royal Society, No. 217, Vol. XXXIII.

Plates prepared by the formula used by Mr. W. B. Bolton exhibit the same phenomena in a less degree than if more iodide be used. The formula stands thus:—

Ammonium bromide	...	...	60 grains
Ammonium iodide	...	...	5    "
Ammonium chloride	...	...	5    "
Gelatine	...	...	10   "
Water	...	...	4 ounces

Two drops of hydrochloric acid (1 : 5) are added, and then—

Silver nitrate	...	...	120 grains
Water	...	...	$\frac{1}{2}$ ounce

Boiling continued for half an hour.

Another excellent formula is to substitute, for the chloride in the above, 15 more grains of ammonium

iodide, and to boil for one and a-half to two hours. The emulsion will be sensitive, and exhibit the properties above alluded to. In both cases from 80 to 120 grains of gelatine must be added (see Chapter XXXVII.) after being soaked in water.

*Warnerke's Modification of the Emulsion Process.*—Mr. Leon Warnerke has recently found that the image produced on a gelatine film is insoluble in hot water if developed by pyrogallie acid (alkaline) development. A little study of the question will show that in the half-tints there must remain a soluble portion, which will be next the glass plate, and this cannot be removed without removing the whole film. Mr. Warnerke has introduced a paper coated with gelatine, from which the film can be removed by transferring it to glass or paper, as in carbon printing. The soluble matter can then be washed away by hot water, and the image alone will remain on the plate, all the transparent parts being bare glass. This, in its turn, can be re-transferred, and so we have a perfect process in which hyposulphite need never be used. Amongst other plans, intensity can be given by applying permanganate to the film, the gelatine causing a deposition of manganic oxide.

*Methods of Packing Plates.*—The method of packing adopted by some dry-plate makers is an intolerable nuisance. They make zig-zags of thick paper, which they stuff between the ends of each plate, or pair of plates; and when a packet is unclosed and a plate taken out, there is an endless bewilderment of paper and glass, each out of place and hard to put right. For our own part, we like Mr. England's plan. He uses little frames of cardboard to place between his plates, and they are just large enough to be flush with their edges. Thus, for our sized plates ( $7\frac{1}{2}$  by 5) we cut strips of card  $\frac{3}{16}$ " wide,  $7\frac{1}{8}$  inches long, and an equal number of strips  $5\frac{1}{2}$ " long. Tough bank-post paper is gummed over with stiff gum, and allowed to dry, and little squares of about

half-inch size cut out. A short piece and a long piece are laid together, or a pair of lines ruled at right angles to one another on a board, and when the square of gummed paper is made to adhere beneath them, and then deftly folded over, two sides of the required frame

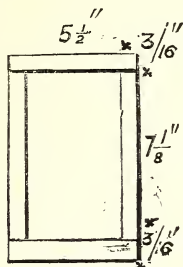


Fig. 17.

were made. One more long, and one more short piece, similarly treated, completed the frame. Four-sheet card is what Mr. England recommends. When the strips are cut, we make about thirty of these frames in an hour. The plates are packed alternately back to back and face to face, in the latter case a frame being placed between them.

Our plates are packed in half-dozens, enclosed in two thicknesses of orange paper. The two packets are enclosed in pieces of black varnished paper, and then placed in boxes.

Boxes made of stiff millboard, and covered with orange paper, are useful. The cover should cover both the top and sides of the box. They should not be too small, but be 1 inch longer and  $\frac{1}{2}$ -inch wider, inside measurement, than the plates. A depth of  $1\frac{1}{2}$  inches will then take one dozen plates. Some makers pack plates with a mere sheet of pure and napless paper between the two films. If the plates are really flat, this plan may be adopted, but then the plates *must* be flat, otherwise the surfaces are apt to get scratched.



*Sensitometers.*—A very useful piece of apparatus supplied by Marion and Co. has been introduced by Mr. Warnerke for testing dry plates. It consists of a piece of glass covered with squares of different thicknesses of pigmented gelatine, each square carrying a number which corresponds to the thickness. The illumination of the plate is made by a phosphorescent tablet, which is rendered luminous by burning a small piece of magnesium ribbon immediately before use. Full directions are issued with these sensitometers. If a plate be exposed it will show on development a certain number. These numbers, when read on a scale, will show the relative sensitiveness of the two plates. By using a sensitometer with the same batch of plates, experiments on developers can be well undertaken. As a guide, we may state that on this standard sensitometer, if the number 14 is shown on development, the plate is slow; if 18, fairly rapid; if 21, rapid; and if 25, very rapid. A wet plate shows, as a rule, the numbers 4 to 6. Each number shows an addition in sensitiveness of about one-third of the preceding number. Plates prepared according to Chapter XXVII. should show the number 25 if kept two days after washing.

Another ingenious sensitometer has lately been brought out by Messrs. Mucklow and Spurge, and consists of a series of chambers which are illuminated by different sized orifices, the area of each bearing some constant ratio to each other.

*Kit for Developing on Tour.*—A small chemical chest is a luxury on tour, but not requisite. All that is absolutely necessary for developing, besides a screen for the candle, is—

6-oz. bottle of concentrated pyrogallie acid.

6-oz.       "                       "       ammonia and bromide.

$\frac{1}{2}$ -lb. of alum.

1 lb. of hyposulphite.

2 oz. of a 20-grain solution of potassium bromide.

2 oz. of a 25 per cent. solution of ammonia.



2 oz. glycerine (useful also for sun burns). .

1 oz. of pyrogallic.

1 oz. measure.

1 drachm measure.

6 trays.

Small ball of string.

A sponge.

A duster.

Gummed paper.

All the above may be packed in a very small box, and  $\frac{1}{4}$  lb. of ferrous sulphate and 1 lb. of neutral potassium oxalate may be taken in addition. A box 10 inches long, 7 inches wide, and 7 deep will hold all of these. Now, all the foregoing, camera included, can be packed in a small basket about 18 inches long by a foot wide and 15 inches deep; and it will be found that no damage of any kind will happen to either plates or bottles, so long as they are fairly tightly packed. The wicker acts as a spring when porters fling the baggage about, as is always the case. Our strong advice is, *always to pack your photographic kit in a basket*. This basket dodge belongs to Mr. England—at least, he first pointed out its advantages, and he invariably adopts it. A two-foot square of india-rubber sheeting is useful during development to save messes on the table, and is utilized in packing to wrap round the boxes of plates to prevent any rain or dust penetrating to them during transit.

*Trays.*—As regards the trays, we believe that tin trays lined with india-rubber sheeting, as adopted by Mr. England, would be better than anything else. Failing these, we would recommend ebonite, but their exposure to the sun should be avoided, since they will soften and flatten out. Another tray is made by turning up the edges of ferrotype plates and bending round the corners. These are cheap, and last some time.

Ordinary *papier maché* trays will answer, but with alkaline development the varnish is apt to dissolve.

Porcelain dishes are usually too uneven in their bottoms to be economical.

*Keeping Gelatine Emulsion.*—When a gelatine emulsion has been prepared for use, and has set, it may be kept an unlimited time by cutting it into lumps of (say) half an inch wide, and allowing it to stand in alcohol; or, after setting in a flask or jar, the alcohol may simply be poured on it, and it will keep free from all decomposition. When required for use, the alcohol is poured off, and the jelly melted in the ordinary manner.

*Increasing the Sensitiveness of Gelatine Plates by Silver Nitrate.*—Dr. Eder and Captain Toth have found the following plan to answer of using silver nitrate with gelatine plates. After the plates are prepared and dried in the usual way, they are laid for from three to five minutes in the following solution, which must be thoroughly filtered :—

Alcohol	...	...	...	12 ounces
Silver citrate solution	...	...	...	1 dr.

The silver citrate solution is made as follows :—

Silver nitrate	...	...	...	50 grains
Citric acid	...	...	...	50 „
Water	...	...	...	1 ounce

The plates are placed on blotting-paper in a place *perfectly free from dust*, and allowed to dry, which they do in a few minutes. The plates are developed by any of the ordinary developers. The sensitiveness is increased three-fold according to the above experimenters.

*Note-Book for Registering Plates.*—In making an expedition during which plates cannot be developed, or when only some can, it is advisable to enter in a note-book all details. We give an extract from a note-book, which will show the form we recommend. It must be premised, however, that each plate, besides bearing the number of the batch, should also bear a distinctive number, which, for convenience, may be written on the same label as that indicating the batch, but using a red pencil instead of blue.

Date.	Hour.	Light.	Slide.	Batch.	Sensitometer Number.	Number of Plate.	Lens.		Exposure.	Subject.	Developed.	Developer.	Remarks.
18/6/81	2.30	G	3	98	26	13	WA*	3	10 sec. Inst. 3-inch opening	River Arun, looking to- wards mill. Lake near Ar- undel, from south.	20/6/81	FO	Use of bromide required in de- veloping. Detail in dark trees of island fairly out.
"	3.10	Cloudy	4	98	26	14	RR†	3			20/6/81	FO	
"	"	"	5	98	26	15	"	"					
"	"	"	6	98	26	16	"	"					
"	"	"	7	82	18	31	"	"					
18/6/81	2.35	G	8	82	18	32	WA*	2	30	Same as 13.	20/6/81	FO	Hypo. used in developer. Detail fair.

\* WA means Dallmeyer's wide-angle landscape lens.

† RR means Dallmeyer's rapid rectilinear lens.

When the slides are filled before starting, the columns filled up are 4, 5, 6, 7, and the rest are filled up after exposure and after development. By adopting this plan, a complete record of every plate exposed and developed is obtained, and will be found of use in judging of exposures.

*Sulphite of Soda in the Alkaline Developer.*—At page 199 it was mentioned that Mr. Berkeley had recommended the use of sulphite of soda with pyrogallic acid. The most recent formula given by that gentleman is as follows:—200 grains of sodium sulphite are first dissolved in 1 ounce of water. When the crystals are dissolved the solution is neutralized by adding a strong solution of citric acid (about 4 grains of citric acid generally suffices); 50 grains of pyrogallic acid are then added. This is about a 10 per cent. solution of pyrogallic acid, and corresponds with formula P, page 191, for which it may be substituted. The solution will remain colourless for months, and paper enlargements may be developed by using it without leaving any stain. It is an excellent formula.

*Dr. Lohse's Preparation of Pure Silver Bromide without Washing.*—Dr. Lohse prepares silver bromide in the usual manner, and after boiling, and before adding the additional gelatine, adds acetic acid to the emulsion. Every 100 grains of gelatine used before boiling requires about  $1\frac{1}{2}$  ounces of acetic acid. The emulsion is then diluted with 20 volumes of water, and allowed to settle three or four days. The bromide settles, and the supernatant liquid may be drawn off. To every 100 grains of silver nitrate originally used 100 grains of gelatine should be weighed out, swelled, and dissolved in  $3\frac{1}{2}$  ounces of water. The bromide is then added and incorporated by shaking in a bottle. The sensitiveness seems to be impaired to a certain extent by this mode of proceeding; but the plates are bright, dense, and clear.

---

ERRATUM.—Page 6, 3rd paragraph, line 15, should read:—"Thus he found 1 grain of the following bromides to require annexed number of grains of silver nitrate."

---

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and Holder, \$8.50; Tripod, \$2.40; Lens, \$5.40.  
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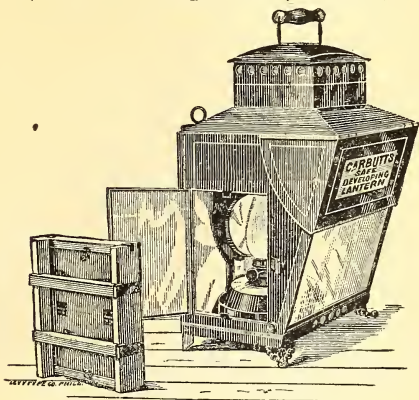
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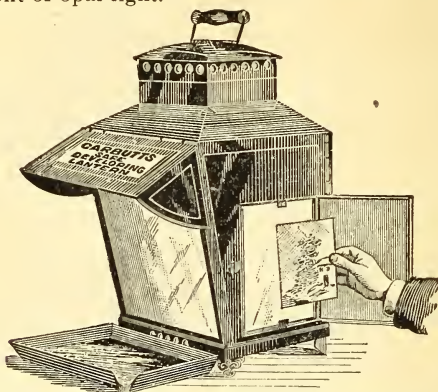
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Note Reduction.		PRICE LIST.	Note Reduction.	
SIZE.	PER DOZ.	SIZE.	PER DOZ.	
3 $\frac{1}{4}$ x 4 $\frac{1}{4}$ inches.....	\$0 65	6 $\frac{1}{2}$ x 8 $\frac{1}{2}$ inches.....	\$2 40	
4 x 5       “ .....	0 95	8 x 10       “ .....	3 60	
4 $\frac{1}{4}$ x 5 $\frac{1}{2}$ “ .....	1 00	10 x 12     “ .....	5 20	
4 $\frac{1}{4}$ x 6 $\frac{1}{2}$ “ .....	1 25	11 x 14     “ .....	6 80	
5 x 6       “ .....	1 35	14 x 17     “ .....	10 00	
5 x 7       “ .....	1 65	17 x 20     “ .....	17 50	
5 $\frac{1}{2}$ x 7      “ .....	1 75	18 x 22     “ .....	20 00	
5 x 8       “ .....	1 85	20 x 24     “ .....	24 00	

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**WILL BE AS FOLLOWS:**

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3 $\frac{1}{4}$ x 4 $\frac{1}{2}$ inches. ....	\$0 65	\$0 72	8 x 10 inches. ....	\$3 60	\$4 00
4 x 5 " .....	0 95	1 04	10 x 12 " .....	5 20	5 80
4 $\frac{1}{4}$ x 5 $\frac{1}{2}$ " .....	1 00	1 12	11 x 14 " .....	6 80	7 60
4 $\frac{1}{2}$ x 6 $\frac{1}{4}$ " .....	1 25	1 40	14 x 17 " .....	10 00	11 00
5 x 7 " .....	1 68	1 85	17 x 20 " .....	16 00	18 00
5 x 8 " .....	1 80	2 00	18 x 22 " .....	18 00	20 00
6 $\frac{1}{2}$ x 8 $\frac{1}{2}$ " .....	2 40	2 70	20 x 24 " .....	22 50	25 00
7 x 9 " .....	3 00	3 40			

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4 x 5.....	“	0.95	10 x 12.....	“	5.20
4½ x 5½.....	“	1.00	11 x 14.....	“	6.80
4½ x 6½.....	“	1.25	14 x 17.....	“	10.00
5 x 7.....	“	1.65	17 x 20.....	“	17.50
5 x 8.....	“	1.85	18 x 22.....	“	20.00
6½ x 8½.....	“	2.40	20 x 24.....	“	24.00

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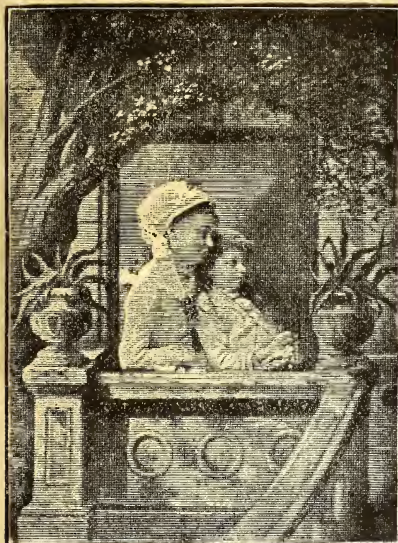
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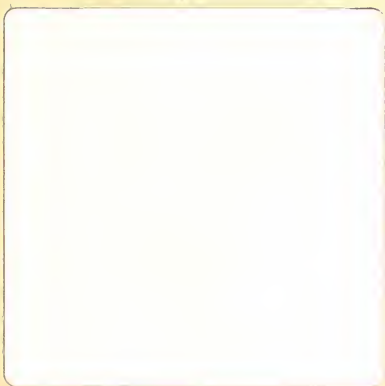
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